THE CATALYTIC HYDROGENATION OF DIMETHYL ACETYLENE

ON

PALLADIUM, GOLD, AND THEIR ALLOYS

by

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TO MY PARENTS

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I was supervised during this period by Dr. D.A. Whan to whom I am indebted for much useful discussion and advice.

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H. G. RUSHFORD

SUMMARY

In this present work the techniques of the high vacuum gas line and of Gas-Liquid Chromatography have been applied to the study of the heterogeneous catalytic hydrogenation of Dimethyl Acetylene (DMA) over catalysts of palladium gold and their alloys.

The palladium catalysts (film wire and foil) exhibited high activity and selectivity for the production of cis-but-2-ene. Hydrogen poisoning was shown to be important and a major problem in obtaining reproducible results.

Gold catalysts (also film foil and wire) were investigated and although their selectivity remained fairly high for the production of cis-but-2-ene under the usual reaction conditions this was not always so. An unexpected hydrogenolysis occurred on gold wires at high temperatures producing C_1, C_2 and C_3 products. Isomerisation of the DMA to the two butadienes occurred on all the gold catalysts. The activity of gold catalysts was always low, however.

The alloy catalysts were always in the wire form, and were difficult to activate reproducibly. Their activities and selectivities varied between those of palladium and gold. The apparent activation energy did not vary much with composition which led to the development of a theory of reaction, involving islands, or clusters, of palladium atoms on the alloy surfaces.

CONTENTS

INTRODUCTION.

1.1 Historical:

Of all the branches of chemistry, heterogeneous catalysis must come closest in spirit to the dreams of the mediaeval alchemists, and their predecessors. This is since the apparently immutable catalyst is brought into contact with a mixture of gases and liquids, and the composition of the mixture changes, leaving the stone, or catalysts, unchanged. Such were the dreams of the alchemists in their attempts to transmute the elements.

Even to-day the process can seem like magic to the layman, seeming to break some law of nature by its very action. In this respect, I well remember my first experience of heterogeneous catalysis and the wonder with which I regarded a few inches of platinum wire begin to glow as it was brought into contact with the vapour above a flask of acetone. To us schoolboys watching it seemed that we had witnessed a great wonder of science.

Perhaps a definition of catalysis should be introduced at this point. The terms catalyst and catalysis were introduced in 1836 by Berzelius (1) and since that date a large number of definitions have appeared. We shall state here though that

i) A catalyst is a substance which increases the rate at which a chemical reaction reaches equilibrium without itself undergoing apparent chemical change.

ii) Catalysis is the word used to describe the action of a catalyst.

iii) To comply with the laws of thermodynamics the above definitions carry the proviso that any equilibrium so attained must be identical to that which would exist if no catalyst was present.

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It will be seen therefore that the catalyst must increase the rates of both the forward and the reverse directions.

Catalytic reactions may themselves be divided into two major classes:

i) Homogeneous catalysis, in which reactants and catalysts exist in the same phase.

ii) Heterogeneous catalysis, in which the reaction takes place at an interface between two phases.

The work discussed in this thesis, is a particular aspect of Heterogeneous Catalysis, involving the reation between two gases on a metallic surface.

The first catalytic reactions known to man were probably of the homogeneous type, even though the mechanism was not understood. An example of this would be alcoholic fermentation which is a biological catalytic reaction involving enzymes. The results of this particular reaction have been known since the dawn of civilisation, even if the mechanism was not understood.

The earliest scientific observations of catalysis seem to have taken place at the close of the eighteenth century and at the beginning of the nineteenth. In 1796 Van Marum (2) reported his discovery that alcohol was dehydrogenated by passage over copper while, in 1812, Kirchoff (3) studied the degradation of starch by dilute mineral acids. The researches of Davy (4) and Döbereiner (5) into the glowing of metals in mixtures of air and combustible gases then lead Berzelius (1) in 1836 to his definition of catalysis.

Berzelius/

Berzelius chose to define catalysis in terms of a special force, the 'catalytic force of bodies' (borrowed from the Greek for "I unloose"). This force was said to lead to an increased yield of products. It is now known, of course, that the most which a catalyst can do is increase the rate at which the reaction approaches its thermodynamic equilibrium but it was only at the beginning of the present century that Ostwald (6) introduced the idea that catalytic action should be measured in terms of reaction rate, and defined a catalyst as "any substance which alters the velocity of a chemical reaction, without appearing in the end products".

One could say that Ostwald gave a quantitative meaning to the qualitative term "catalysis", introduced by Berzelius.

1.2 Heterogeneous Catalysis:

The study of heterogeneous catalysis has continued from those times and has been the subject of much experimental and theoretical work, although the experimental facet of the subject has tended to progress at a much greater rate than theoretical studies.

Let us rigorously define heterogeneous catalysis: this occurs whenever the rate of a chemical reaction is enhanced by the presence of an interface between two phases. Heterogeneous catalysts are materials which increase the rates of chemical reactions, by virtue of the specific properties of their surfaces.

The first simple hypothesis attempting to explain these properties, assumed that the mere mechanical impact of the molecules, with the solid surface, caused chemical activation. This explanation was quickly ruled out however, in view of the high specific action of different surfaces.

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An alternative theory, proposed by Faraday (7), stated that the activity was due to the attraction of the surface for gas molecules, which concentrated them near the surface, thus causing them to react more readily. Mitsherlich (8) termed this "contact action" and described elements which are similar to some modern theories of reaction in a chemisorbed layer. It did not, however, really explain the specific nature of catalytic reactions, and this led to Sabatier (9) in 1913, introducing the idea of unstable intermediate compounds adsorbed on the catalyst surface, when he proposed that surface nickel hydride was an intermediate in the catalytic hydrogenation of ethylene.

Langmuir's (10) work on the adsorption of gases by metals was a great boost to this theory. Langmuir showed that not only did metal surfaces adsorb gases, but that the amount of adsorption increased with increasing pressure until a constant maximum was reached. This lead him to conclude that the adsorbed molecules were held by essentially chemical bonds, and that the amount of adsorption depended on the number of surface sites available. Clearly, then, adsorption is of great importance in the consideration of catalytic reactions, and a discussion of the various types of adsorption will be needed.

1.3 Adsorption:

It seems probable that the adsorption of gases on solid surfaces can be split into two types, namely "Physical" Adsorption and "Chemisorption".

i) Physical Adsorption (11)

It could be considered that Physical Adsorption is similar in nature, and in mechanism, to the condensation of vapour on a film of its own liquid in that the forces which bind the molecules of/

of gas to the surface, are similar to those which bind the liquid together, i.e. Van der Waal's forces. Measurements of heats of adsorption have been made and are low and usually in the neighbourhood of the latent heats of condensation of the gases, usually decreasing with coverage. It also appears that Physical Adsorption is impossible much above the critical temperature, and occurs best when close to the boiling point of the adsorbate. There is no activation energy, which entails that physical adsorption is both quick and reversible, even at very low temperature.

The forces to which physical adsorption are attributed are physical, therefore non specific, and the energies involved are small. This would suggest that it is unimportant in catalytic processes, except in so far as it preceeds chemisorption. There are some reactions however, in which it probably does play a part: these will be discussed later, especially with regard to gold catalysts.

ii) Chemisorption:

Chemisorption (12) occurs when a redistribution of electrons, occurs between surface atoms and adsorbed molecules with the resulting formation of a "chemical" bond. As might be expected, the heats of chemisorption are usually much greater than the heats of physical adsorption, i.e. heats of chemisorption usually range from 85 to 250 k.j. mol^{-1}. Because of this, rates of desorption may be small and chemisorption is in many cases irreversible. This particular state of adsorption must obviously then be confined

to/

to a "monolayer" of atoms or molecules on the surface and will be specific in nature. It is considered that chemisorption, and the resulting energy change in the molecule, is essential for at least one of the components of a catalytic reaction although it is possible that other, physically adsorbed, species may take part in the reaction. Another criterion for an efficient catalytic process is that the strength of the adsorption must lie within certain limits; a too strongly adsorbed reactant may be so stable as to be almost impossible to remove (i.e. it will act as a poison), while, if it is too weakly adsorbed, the rate of desorption may greatly exceed the rate of reaction. In view of its obvious importance, much study has been devoted to the process of chemisorption and the chemisorbed state; the more important aspects have been discussed and reviewed by Gundry and Tompkins (13).

It has been shown, using thetechniques of Infra-Red Spectroscopy (13,14) and Electron-Spin Resonance (15) that a chemisorbed gas may form a number of species, often highly rearranged, and that the relative proportions of these species may be strongly affected by the presence of another gas.

Hence, care must be taken in the correlation of data from this source, with catalytic reactions. Kemball (16) has shown that species with a very low coverage (e.g. 0.1%) can be catalytically important provided, obviously, that its rate of formation, subsequent reaction and desorption are rapid.

1.4/

1.4 Mechanism in Heterogeneous Catalysis:

The heterogeneous catalytic reaction in the gas phase, can usually be split up into five simple steps:

i) Diffusion of the molecule(s) from the gas phase to the surface.

ii) Chemisorption on the surface (possibly via physical adsorption).

iii) Chemical reaction of the chemisorbed species with either

a) other chemisorbed species

b) physically adsorbed molecules

c) molecules colliding with the surface.

iv) Desorption of products.

v) Diffusion of products into the gas phase.

The rate of reaction will be controlled by the slowest of these steps. Normally (i) and (v) would be unlikely to influence the reaction rate, at the pressures used in the laboratory. In very fast reactions, however, or in reactions where desorption of reactants is fast, they may be of importance. Since diffusion processes are not greatly dependent on temperature, whereas chemical reactions are, an Arrenius Plot which gives a straight line would indicate that diffusion processes are not important.

The stages of the reaction covered by (ii), (iii) and (iv), however, are chemical in nature and any one of them would normally be the rate limiting step.

A number of methods have been used for the determination of the rate limiting step for a reaction, e.g. if a reaction appears to be zero order throughout its whole range then the rate limiting step is probably the slow reaction of a strongly chemisorbed species.

Analogous/

Analogous and related reactions may be used; Kummer and Emmett (17) showed that the rate of exchange between $^{28}N_2$ and $^{30}N_2$ was very similar to the rate of formation of ammonia from nitrogen and hydrogen. They thus concluded that the rate limiting step, in the formation of ammonia, was the chemisorption of nitrogen (with the associated splitting of the nitrogen-nitrogen bond).

Mechanism for the actual catalytic reaction, between two molecules, fall into two categories;

i) Those in which both reacting species are chemisorbed, i.e. the Langmuir-Hinshelwood mechanism (18,19). In this case the rates of adsorption and desorption are assumed constant so that the reaction rate depends on the reaction between the adsorbed species. For instance, in the case of hydrogen-deuterium exchange, the rate limiting step would be the combination of the separate Hydrogen and Deuterium atoms on the surface. This probably applies best to reactions at higher temperatures where it is reasonable to suppose that adsorptions and desorptions proceed fairly rapidly. Roberts (20) however, has shown that although hydrogen adsorbs on Tungsten at -80°C, its desorption is rather slow even at 400°C. This obviously does not fit with the above reaction scheme and led to Eley and Rideal (21,22) proposing an alternative mechanism.

ii) The Eley-Rideal mechanism proposes that only one species is chemisorbed and that it reacts directly with a molecule in the gas phase, or with a physically adsorbed molecule.
Thus a physically adsorbed deuterium molecule would react with a chemisorbed hydrogen atom yielding an H-D molecule, physically adsorbed, and a chemisorbed deuterium atom.

Just which mechanism is occurring is difficult to determine from kinetic evidence, although spectroscopic studies of surface species can yield clues as to the nature of the surface mechanism,but these are difficult to interpret.

Work using deuterium and other isotopic tracers can be more useful, and work in this field has been well reviewed (23, 24, 25, 26, 27).

1.5 The Geometric Factor is Catalysis:

A large number of attempts have been made to correlate the activity of a solid surface, its geometry, and the stereochemistry of the reactants. The suggestion being that if the array of surface atoms has a good geometric fit with a reacting species, particularly when this fit perhaps involves the species being held in a favourable conformation for the subsequent reaction, then the catalyst will be particularly active for that reaction. Although some success has been achieved using such correlations they have been useful, mainly, when dealing with large reactant molecules in which the steric effect would be expected to be significant. Olefin hydrogenation in heterogenous systems has been reviewed, with respect to stereochemistry, by Siegel (28) and by Bondand Wells (29).

Obviously though, factors such as specific surface area, and surface topography must be considered. A fairly redent discussion of the current standing of the geometric factor is that by Thomas and Thomas (30).

1.6 The Electronic Factor in Catalysis:

The idea behind the so called "electronic factor" in catalysis is that the activity of a catalyst is, in some way, connected to its bulk electronic properties whether it be a metal, alloy or semi-conductor. It is well known that transition metals are, in general, much more active catalytically than non/

non-transition metals. Theoretically it is very convenient to connect this activity with the vacancies which occur in the d-band of the transition metals since, according to the band theory (31,32), the electrons in metal retain much of the character which they possess in isolated atoms. Instead of discussing discrete, single valued energy states for the s,p and d electrons, however, we must consider the bands of permitted energy values which occur in the metal crystal. These bands correspond more or less to the discrete orbitals of the isolated atom, although the distribution of electrons through them may differ and they may also over-lap; this is a major cause of electron redistribution. Frequently this redistribution occurs when electrons which, in an isolated atom, would be in an outer s-band are donated to the unfilled d-band of a transition metal. The remaining vacancies in the d-band are referred to as d-band holes. According to Pauling (33) these vacancies become non-bonding, atomic d-orbitals, into which electrons can be donated. Boudart, shortly afterwards noted the correlation between the catalytic activity of transition metals for ethylene hydrogenation and their percentage d-character (34), Schwab (35) and Kemball (36) also noted correlations between percentage d-character and activation energy.

It can be pointed out of course that the geometry of a crystal is dependent on its electronic structure thus making the "geometric" effect merely a side effect of the "electronic" effect. This cannot, however, account for the varying activity of the different crystal faces of the same metal.

Ehrlich (37) has pointed out that if there is a correlation between selectivity for hydrogen and d-band holes, then we should employ the binding energies of hydrogen <u>atoms</u>, not molecules, to the elements. When these figures/

figures are studied there does not seem to be any correlation. Indeed some elements which have no d character form quite strong bonds yet they are unable to chemisorb molecular hydrogen. Those atoms which can chemisorb molecular hydrogen however, have a binding energy for a hydrogen adatom which exceeds one half of the dissociation energy of the hydrogen molecule. These, it is true, are almost all of d-character but the differences in hydrogen atom binding energy for these, and some "sp" metals, is quite small.

Nevertheless, the correlation between the d-character and catalytic activity of some polycrystalline metals and alloys exists, particularly for some alloys. These will be discussed later. The electronic factor has been discussed extensively by Stone (38), Bond (39) and Thomas and Thomas (30).

1.7 The Catalytic Hydrogenation of Acetylenes:

One of the earliest reports of the heterogeneous catalytic hydrogenation would appear to be that of Sabatier and Senderens in 1899 (40) and a number of reports of work on this topic were published over the years until the 1940's when Sheridan (41,42,43,44,45) published his work which, it could be said, began the modern study of the topic. The progress which has been made in the twenty years between 1944 and 1964 has been covered thoroughly, by Bond and Wells (46), in a review which outlines clearly what was known at that time of the gas-phase catalytic hydrogenation of acetylenes, including the high selectivity for olefin products, and where it is possible, the high selectivity for particular stereoisomers. There was, however, at that time a great lack of information concerning the adsorbed state of acetylene; this is even now a sphere of conjecture. It/

It was recognised however, that for most metal catalysts, particularly those of the transition series, the reaction in question was first order in hydrogen and zero or slightly negative with respect to acetylene. The nature of the catalyst would appear to be important as regards selectivity, supported nickel catalysts, for example, tending to give a high degree of acetylene polymerisation. The relative concentrations of acetylene and hydrogen can also affect the degree of selectivity quite strongly. Reaction profiles also tend to vary considerably with initial hydrogen/acetylene ratio and with the catalyst, its pretreatment and the order of addition of the reactants, low hydrogen/acetylene ratios tending to give first order curves, and high ratios, zero order curves.

1.7a Reaction Mechanism:

It seems likely, in the light of evidence which will be discussed later, that the addition of hydrogen to adsorbed acetylene, proceeds in a stepwise fashion so that the simplest mechanism which can be proposed is as follows:

$$H_2(g) \underset{(2)}{\overset{(1)}{\rightleftharpoons}} 2\ H^{*}$$

$$C_2H_2(g) \xrightarrow{(3)} HC{\equiv}CH^{**}$$

$$HC{\equiv}CH^{**} + H^{*} \underset{(5)}{\overset{(4)}{\rightleftharpoons}} HC^{*} = CH_2$$

$$HC^{*} = CH_2 + H^{*} \xrightarrow{(6)} H_2C = CH_2^{*}$$

$$H_2C = CH_2^{*} \xrightarrow{(9)} C_2H_4(g)$$

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An alternative step, however, involves the reaction of two adsorbed vinyl radicals which may disproportionate i.e. step (5) above

$$\underset{* \ *}{+ \ 2 \ HC = CH} \xrightarrow{(7)} \underset{**}{HC \equiv CH} + \underset{*}{H_2C = CH_2}$$

Therefore, assuming that a "steady state" exists on the surface, and equating the rates of formation and disappearance of adsorbed vinyls

$$k_4 \, \theta_{C_2H_2} \, \theta_H = k_5 \, \theta_{C_2H_3} + k_6 \, \theta_{C_2H_3} \, \theta_H$$

Now, if the vinyl reversal is much more rapid than vinyl hydrogenation

$$k_5 \gg k_6 \, \theta_H$$

Therefore

$$\theta_{C_2H_3} = \frac{k_4}{k_5} \cdot \theta_{C_2H_2} \, \theta_H$$

Now the rate of ethylene formation "r" is given by

$$r = k_6 \theta_{C_2H_3} \, \theta_H$$

$$\therefore r = \frac{k_4 k_6}{k_5} \, \theta_{C_2H_2} \, \theta_H^2$$

i.e. the reaction will be first order in hydrogen and zero order in acetylene

$$\text{if } \theta_{C_2H_2} = \text{const} \rightarrow 1$$

It is possible however that over such metals as nickel and palladium, that hydrogen adsorption is irreversible. Therefore as the rate of hydrogen adsorption will be proportional to the hydrogen pressure then so/

so must the rate of formation of adsorbed vinyls, assuming vinyl disproportionation to be the important route for ethylene formation

$$k P_{H_2} = k_7 \theta_{C_2H_3}^{\ 2}$$

$$= r$$

i.e. the reaction is first order in hydrogen.

This cannot be the whole story however, as some orders in hydrogen of approximately 1.5 have been recorded (47,48). It seems probable that, to explain this, an alternative route involving an adsorbed hydrogen molecule may be considered.

$$\begin{array}{l} HC = CH_2 \\ | \\ * \end{array} \quad \begin{array}{c} H_2 \\ \vdots \\ + \ * \end{array} \xrightarrow{(8)} \begin{array}{l} H_2C = CH_2 \\ | \\ * \end{array} + \begin{array}{l} H \\ | \\ * \end{array}$$

From the earlier mechanism we can say that

$$\theta_{C_2H_3} \propto P_{H_2}^{\ 0.5}$$

and from the above

$$\frac{d}{dt}(P_{C_2H_4}) = k_8 \theta_{C_2H_2} \theta_{C_2H_3} P_{H_2}$$

$$\therefore \frac{d}{dt}(P_{C_2H_4}) \propto P_{H_2}^{\ 1.5}$$

i.e. the reaction is of order 1.5 in hydrogen.

1.7b Selectivity Factors:

The unusually high selectivity which most catalysts display for the hydrogenation of acetylene has been attributed to two factors (49); the thermodynamic and the mechanistic. Considering the thermodynamic factor, with/

with relation to two gases, X and Y, we may write

$$\theta x = kxPx/(1 + kxPx + kyPy)$$

and $$\theta y = kyPy/(1 + kxPx + kyPy)$$

where θx and θy are the respective coverages

Px and Py are the respective pressures

kx and ky are constants

Let Gx and Gy be their respective free energies of adsorption

then

$$\delta\Delta G = \Delta G_x - \Delta G_y$$

$$= -RT \ln (kx/ky)$$

hence $$\frac{\theta x}{\theta y} = \frac{Px}{Py} \cdot \exp (-\delta\Delta G/RT)$$

This means that $\delta\Delta G$ does not need to be very large before the more weakly adsorbed gas will be effectively barred from the surface. Since all observations to date indicate that olefins are less strongly adsorbed than the corresponding acetylenes, this must exert a very strong influence on the observed selectivity.

It is obvious that another important factor must be the mechanistic one; that is, the inherent activity of the catalyst for the hydrogenation of the olefin, with respect to its activity for acetylene hydrogenation, must be considered.

The general agreement is good (46), metals with high activity for ethylene hydrogenation certainly tend to be less selective in their hydrogenation of acetylene. Palladium is a noticeable exception, due obviously to the thermodynamic factor being particularly strong, while osmium and iridium must have particular weak thermodynamic factors since, despite/

despite their low activity for ethylene hydrogenation, they display a low selectivity for acetylene hydrogenation.

1.7c The Experimental Evidence.

The work of Bond and Wells on acetylene hydrogenation, using alumina-supported palladium and platinum catalysts (47,48) has already been mentioned.

This has been extended by Bond and Wells (50,51) and by Bond, Webb and Wells (52), who have studied the reaction of acetylene with hydrogen over alumina supported rhodium and iridium, the deuteration of acetylene over rhodium, palladium, iridium and platinum, and the hydrogenation and deuteration of acetylene over alumina-supported ruthenium and osmium.

This work follows on from that of Sheridan and Reid (53) and Sheridan and Bond (54,55,56) on polyunsaturates which did itself succeed the previously mentioned work of Sheridan (41-5).

The general conclusions of this work are as follows:

i) The order of the reaction in hydrogen is 1 or 1.5; this can be explained by assuming that hydrogenation occurs via a stepwise addition of hydrogen atoms to the chemisorbed acetylene utilising either chemisorbed hydrogen atoms or physically adsorbed hydrogen molecules.

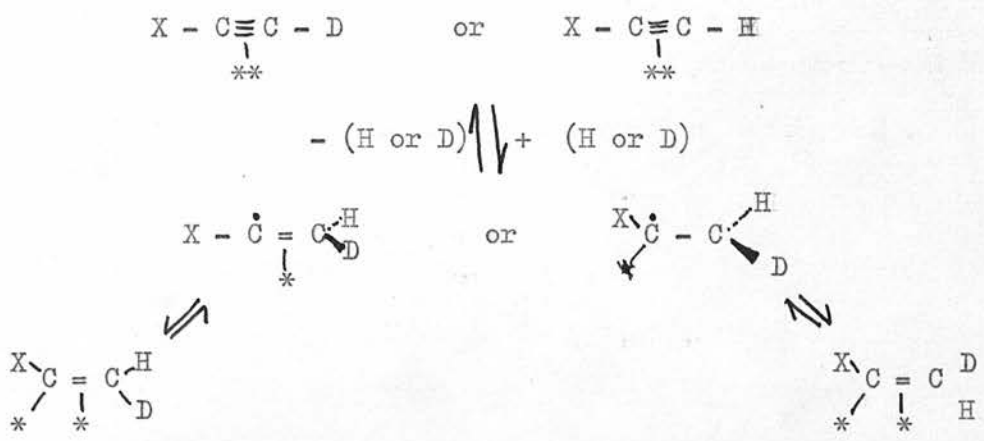
ii) The order in acetylene is zero or slightly negative; it may be presumed that for those catalysts on which it is zero, the relatively weakly adsorbed hydrogen is not competing for the same sites as the acetylene but that on the catalysts for which the/

the order is negative the two species are competing and that possibly hydrogen is only permitted to adsorb on those sites which the geometry of the surface packing of the bulky acetylene molecules leaves vacant.

iii) From the above evidence, and as a result of the previously mentioned deuteration studies (51,52), the mechanism for the heterogeneous catalytic hydrogenation of acetylene over the platinum metals is almost certainly a stepwise addition of hydrogen which is certainly reversible in the intermediate stage, as indicated by the extensive smearing of deuterium through the product ethylene (although this effect varied markedly with catalyst). Studies of the structure of ethylene-d_2 showed that, although all three possible isomers were found, usually only a trace of the asymmetric species occurred while the ratio of the cis to transisomers varied from over four to almost one. High selectivity for the d_2 product tended to coincide with high selectivity for the cis product (palladium and platinum), while low selectivity for ethylene-d_2 coincided with the cis trans ratio of almost one and a high asymmetric d_2 yield (15% for rhodium).

It seems likely that these facts can be correlated by postulating the isomerisation of adsorbed ethyl radicals and comparing the relative rates at which the competing steps may occur.

x-c/



As a result of this work, Bond (57,63,64) introduced two parameters, which he designated s and p, further discussed by Bond and Wells (51), which can be used to describe the probabilities of the half hydrogenated species either reverting to an adsorbed acetylene species, or being further hydrogenated to an adsorbed ethylene molecule.

S = probability of an adsorbed acetylene gaining a deuterium atom.

(1 -S) = probability of acetylene gaining a hydrogen atom.

P = probability of vinyl species being hydrogenated to ethylene.

(1 -P) = probability of vinyl species losing hydrogen or deuterium, and reverting to acetylene.

Using theoretical values of s and p, theoretical deuterium distributions in product ethylene may be calculated and compared with those obtained; generally, good correlation was obtained.

The earliest report of acetylene hydrogenation on alloy catalysts seems to be that of Bond, Dowden and Mackenzie (58) who investigated the/

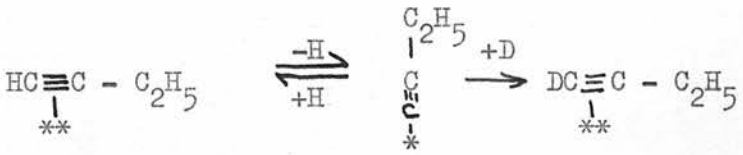
the reaction using alumina-supported rhodium, palladium, platinum and palladium/silver alloys. They noted the high activity of alloys containing 10 - 30 atoms % silver and the poisoning effect of hydrogen on the catalyst. It appeared that palladium pre-exposed to hydrogen was poisoned with respect to the acetylene reaction and totally inactive for ethylene hydrogenation.

1.7d The Catalytic Hydrogenation of Alkylated Acetylenes:

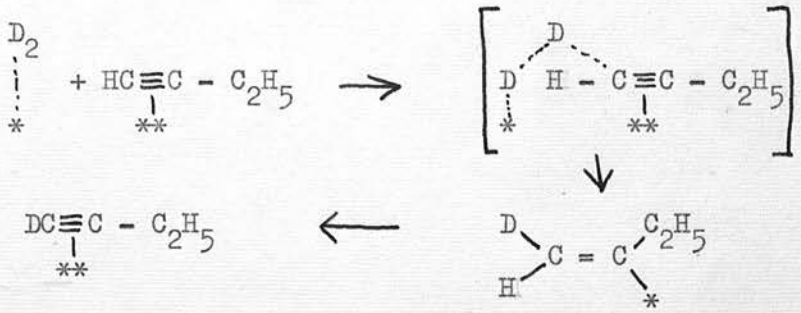
The catalytic hydrogenation of alkyl and dialkyl acetylene is obviously of more direct interest to the work in hand. Little work has been published on the gas phase reaction, primarily it would seem because only three of them are gases, or of sufficiently low boiling point to be considered as gases under normal experimental conditions. These three are propyne, 1-butyne and 2-butyne (dimethyl acetylene). Some of the earliest work in this field is that of Bond and Sheridan (55) who described the hydrogenation of propyne on pumice-supported nickel, palladium and platinum. These all gave a reaction which was first order in hydrogen and zero or slightly negative order in propyne, the product being highly selective for propylene.

Meyer and Burwell (59) have reported the gas phase catalytic hydrogenation of 1-butyne, over aluminina-supported palladium, to give a 99% yield of 1-butene with only traces of other butenes and butane, indicating that isomerisation of the reactant to dienes must be slow under the prevalent conditions. Deuteration studies showed some exchange of the acetylenic portion of the reactant; while the 1-butene product was mainly of the d_2 type, 12% and 14% of the d_3 and d_1 forms were also found/

found. No substitution of the ethyl group was observed. As a result of this work, they suggested a mechanism of the following type to explain the acetylene exchange:



An alternative and more attractive mechanism, however, which would agree better with Bond and Wells work for acetylene hydrogenation over supported catalysts (47,48) is as follows:



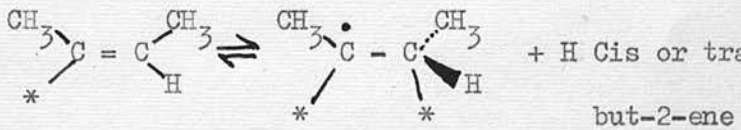
Burwell has also, along with Hamilton (60) and Meyer (61) again, studied the hydrogenation and deuteration of but-2-yne, in the gas phase, using alumina-supported palladium catalysts. Simple hydrogenation (60) gives large yields of cis-but-2-ene and, when the catalyst has reached a steady state, is virtually the only product until all the but-2-yne has been reacted, at which point, isomerisation of the butene to near the thermodynamically stable ratio of butenes occurs, accompanied by slower hydrogenation to butane. Deuteration of the but-2-yne (61) yields, almost exclusively, cis-2-butene, 2,3d_2 other butenes and butane total only 1%. When a mixture of hydrogen and deuterium is used no H -D exchange is observed and the distribution of cis-2-butene-d_o, -d_1 and d_2 is random, apart/

apart from an incorporation isotope effect of 1.6 favouring hydrogen. Thus hydrogen is adsorbed dissociatively.

The evidence here then would suggest a simple stepwise addition of H or D atoms.

The work of Phillipson et al (62) on the hydrogenation of but-2-yne over alumina supported Group VIII metals and over copper gave a more complex range of products, but the results were basically similar.

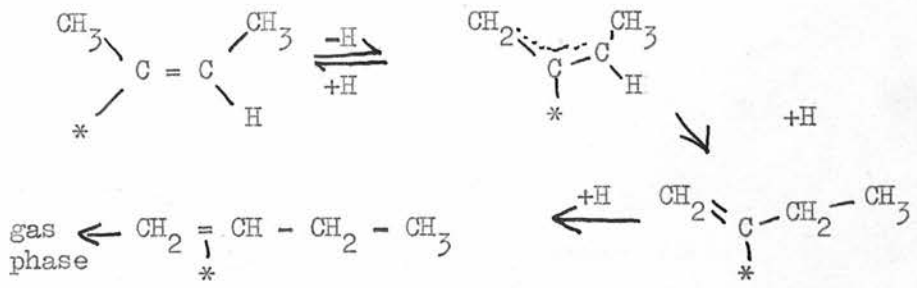
The metals used were iron, cobalt, nickel, copper, rhodium, iridium, and platinum which all showed a high selectivity for olefin production, but cis-but-2-ene was far from being the only product, trans-But-2-ene and but-1-ene were also produced, and over rhodium and iridium 1,2 butadiene was also produced. Deuteration studies showed that the but-2-enes were predominantly of the expected d_2 type, but-1-ene however showed considerable amounts of the d_3 variety also. Since the cis/trans ratio seems to be almost independent of initial pressures, and temperatures, it would seem that a separate mechanism may be at work, possibly



The but-1-ene is probably formed by the hydrogenation of an adsorbed 1,2 butadiene species since 1,2 butadiene is sometimes observed as a product

i.e./

i.e.



This would explain the occurrence of the d_3 product.

Again, the olefins tended to isomerise to the thermodynamic ratio, after the acetylene had all reacted, along with further hydrogenation.

In recent years the most prolific worker in the field of the catalytic hydrogenation of alkyl acetylenes is Mann who had collaborated with Bond on some of his work on the hydrogenation of acetylenes over nickel catalysts (63). He began by studying with Naik (65), the gas phase hydrogenation of methyl acetylene over supported and unsupported nickel. He continued the work in collaboration with Khulbe (66,67,68,69,70) over unsupported nickel, iron and cobalt, unsupported nickel, cobalt and copper, copper-nickel alloys, supported palladium, platinum, iridium, rhodium and ruthenium, and most recently platinum and iridium. Generally speaking, the pattern which emerged was similar to that for simple acetylene. The reactions were always first order in hydrogen and zero or slightly negative in methyl acetylene. The reaction was usually highly selective for propylene, yielding also small and variable amounts of propane and reduced methyl acetylene polymers. The only exceptions were copper, and copper-nickel alloy catalysts of high copper content, over which the order in methyl acetylene was positive and tending towards 0.5 for pure copper (67,68). It is possible to account for the/

the activity of the alloys on the basis of d-band theory (see later). The evidence here is generally for a stepwise addition of adsorbed hydrogen atoms to the adsorbed acetylene, reaction with physically adsorbed hydrogen molecules, may well be hindered by the large methyl group.

Mann and Khulbe have also studied the hydrogenation of ethylacethylene (but-1-yne) over nickel pumice, unsupported nickel, cobalt and iron, and over supported and unsupported platinum and iridium catalysts, (71,72,73).

The results obtained were generally as expected: usually the reaction is selective for 1-butene with only small traces of other butenes, butane and polymers. The reaction is always first order in hydrogen and zero in ethyl acetylene, tending to become negative, particularly as temperatures increase. The exception is iridium. The supported form of the catalyst has an unusually low selectivity and iridium powder is not very selective at all. It is probable that the mechanistic factor (49) is of great importance relative to the thermodynamic of this case. The evidence is again in favour of the stepwise addition of adsorbed hydrogen atoms although in the case of iridium, alternative routes may be operating. Polymerisation may occur, as with other acetylenes, via an adsorbed vinyl radical.

The work of Webb and Wells (74) on the hydrogenation of but-2-yne over alumina-supported ruthenium and osmium falls once more into the usual pattern with regard to ruthenium, which is typical of its class of metals as an acetylene hydrogenation catalyst. Osmium however, like iridium it would seem (73), is rather different in that its selectivity for olefin production is rather low; in that almost 20% of the initial product is butane/

butane. As on iridium, the mechanistic factor must be particularly important.

The conclusions which can be drawn from this work are simple and few. They are that strongly adsorbed acetylenes are hydrogenated stepwise and generally highly selectively to the corresponding olefins and where stereoisomers of the olefins are possible, selectively for particular stereoisomers also. The hydrogen, which is less strongly adsorbed, may react via an adsorbed molecule or a chemisorbed atom and which of these predominates may be determined by kinetic studies. There is little evidence concerning the adsorbed state of acetylenes; all that can be said, is that they are adsorbed in a cis configuration, or that some reaction intermediate must take up a predominantly cis configuration. This is a field in which much work remains to be done.

1.8 The Palladium - Gold Alloys; and their Catalytic Activity.

The palladium gold alloys are a complete series of substitutional, single phase f.c.c. alloys. The rise in lattice spacing is very small 3.88 to 4.07 Å and there is no evidence of a miscibility gap (76). They are thus preferable, for catalytic studies, to the related copper nickel alloys where evidence for phase separation exists (77,78,79). The attractiveness which the palladium-gold series holds for catalytic work stems, basically, from the electronic properties of the bulk alloys which allow, over the series, for the effects of two separate electronic properties to be studied, namely:

i) The effect of d-band vacancies.

ii) The effect of a rapidly changing Fermi level.

These, along with catalytic activity, have been reviewed by Eley who, with several co-workers, has studied the catalytic activity of the alloys '80).

The/

The outer electronic structure of palladium (or any similar metals) in the bulk state is, according to Mott and Jones (81) complicated by the overlapping of the narrow "n" d-band and the broad (n + 2) s-band /or (n + 1) s-band for silver say/ which can lead to deviation from the outer d^{10} configuration expected in an isolated palladium atom. Physical evidence from atomic susceptibility measurements (80) would indicate that the outer structure is in fact $d^{9.4} s^{0.6}$ in bulk palladium, i.e. there are 0.6 holes per palladium atom, or perhaps more correctly 0.45 holes in the d-band and 0.15 holes in the s-band, because of the overlap (82). This figure of 0.45 corresponds to some more recent measurements (83) which give the number of d-band vacancies as 0.36 holes per atom.

A more modern theoretical treatment (84) indicates a broad 3d-band hybridised with s and p orbitals and possessing two maxima. Since, however, the Fermi levels of metals such as nickel, palladium and platinum lie above the higher narrow maximum the general behaviour is similar to that predicted earlier on the narrow nd band model.

It is enough for current purposes, however, to say that as atoms containing available "s" electrons are added to palladium, the "d" vacancies will be filled by the "s" electrons (which may come from hydrogen, silver or gold for example). Again, physical measurements (80) show that at approximately 60 atoms% of hydrogen, silver or gold, the d-band vacancies are filled. During this period the Fermi level of the alloys, which lies among the densely packed energy levels of the d-band, changes hardly at all; when the d-band is filled, however, at the 40:60 alloy, the Fermi level changes to the broad s-band in which the density of permitted energy levels is/

is not great, and begins to rise linearly and rapidly. This means that, in the palladium-gold series, we can study the effect of d-band vacancy, over alloy compositions from 0 - 60 atoms% gold, and Fermi level effects over the remainder of the series.

The catalytic activity of the palladium-gold alloys, in the wire form, has been studied by Eley and his co-workers (85,86,87,88), who have studied parahydrogen conversion, the decomposition of formic acid, the oxidation of carbon monoxide, and the decomposition of nitrous oxide.

The parahydrogen conversion, it is suggested (85) can proceed via two mechanisms:

$$pH_2 + HM \rightarrow MH + oH_2$$

which is favoured on palladium rich alloys, and

$$pH_2 + 2M \rightarrow 2MH \rightarrow oH_2 + 2M$$

which is favoured on gold rich alloys.

Rienacker and co-workers have investigated the problem on copper-platinum (89) and copper-palladium (90) alloys with similar results.

The palladium-silver alloys, as catalysts in the same reaction, have been extensively studied as films (91), wires (92) and as foil (93).

The general idea is that the d-band vacancies stabilise the reaction intermediates, whatever the reaction mechanism. Broadly speaking the above investigations have shown that apparent activation energies change little over the 100% - 40% Pd (or Pt) range but rise sharply after this. Two interpretations may be offered

i)/

i) d-band vacancies, however few, will stabilise the reaction path; when there are no such vacancies then much more energy will be required to push the reaction along.

ii) Fermi Level is all important in deciding the activation energy of the reaction.

On a palladium-hydrogen system containing 8 atoms % Hydrogen, the apparent activation energy was 46.2 kj mole $^{-1}$ compared with 12.6 kj. mole $^{-1}$ for pure palladium. The work of Schotten and Konavalinka (94) on the equilibrations of various combinations of ortho and para-hydrogen and deuterium confirm this and indicate that mechanism may depend on the phase in which the catalyst exists.

Exchange between methane (d) and deuterium has been studied by McKee using alloy powders (95) when a similar pattern of activation energy and activity was observed. It is suggested that the decrease in activity when the concentration of gold exceeds 60 atoms % is due to the inability of the alloy to chemisorb hydrogen at the ambient temperatures whereas, below this figure, the alloys can do so copiously (96).

The above studies, as well as the similar work of Wood and Wise (97) and Alchundzhan and Mantikyan (98) usually show a slight increase in activity as up to 30 atoms % gold are added, this is attributed to a slight decrease in bonding energy, making the adsorbed surface layer more labile. (See Bond (23), p. 171.)

The study of the hydrogenation of 1,3-butadiene on pumice supported palladium-gold catalysts by Joice et al (99) is of great interest, since it provides/

provides evidence once more (94) of change of catalytic properties in the solid phase palladium-hydrogen system as the phase of the palladium-hydrogen changes, in this case by a change in product distribution. Maxima in trans-but-2-ene and butane and a minimum in but-1-ene production, were noted at temperatures which coincided with the α-β phase shift at ambient hydrogen pressures. It was suggested that this was due to the ready availability of extra surface hydrogen species under these conditions.

The dehydrogenation of formic acid by palladium-gold catalysts has been studied by Eley and Luetic (86) using wires, and by Clarke and Rafler (100) on alloy films. Their results for gold-rich alloys are remarkably similar: there are, however, differences at the palladium rich end of the scale. It was proposed that this was due to varying textures of the films, resulting in variance in the predominance of particular crystal faces. In both cases, however, apparent activation energy increased slowly over the range 100 - 40% gold, for wires and sintered films. The value then remained constant over the range 100 - 60% palladium. For unsintered films the apparent activation energy rose sharply at 60% palladium then levelled off (see above).

The transition point then seems to occur in the region 60% palladium, compared with 40% for parahydrogen conversion. Eley and Luetic (86) attribute this to the necessity for a "multiple" adsorption site for the formic acid. Inami, Wood and Wise (124) have shown that for the isomerisation of 1-butene to 2-butenes on microsphere palladium-gold alloys, hydrogen is necessary on all alloys and on palladium, but not on gold on which the isomerisation will proceed spontaneously at over 300°C. The presence/

presence of oxygen completely suppressed isomerisation and led to the formation of butadiene on alloys of gold content up to 60 atoms %. They also showed that isomerisation proceeds more quickly than hydrogenation and that both processes depend upon the surface density of hydrogen atoms, indicating that as a primary step in isomerisation the addition of a hydrogen atom is quite probable. Presumably the oxygen, below the 60 atoms % gold level, becomes too strongly bound to the surface. Oxygen is not chemisorbed by gold but can presumably abstract surface hydrogen atoms.

A number of reactions involving oxygen and oxidation have been studied on these catalysts. Daglish and Eley (87) have studied the oxidation of carbon monoxide on wire catalysts. The apparent activation energy is least for pure gold, and greatest for pure palladium, with a sharp rise at 60 atoms % gold. It is suggested that in oxidation reactions an electron transfer from the metal may be involved (101); unlike hydrogenation reactions, in which an electron would be donated to the metal. Despite this, the reaction is slowest on gold rich alloys and it is probable that gold has very few active sites compared to palladium.

Eley and Knights (88) have studied the decomposition of nitrous oxide on alloy wires.

$$\text{i.e. } N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

The apparent activation energy and activity fall sharply over the alloy range 100 - 40 atoms % palladium, but when corrected for heats of adsorption, the true activation energy is seen to be fairly constant from 0 to 50 atoms % gold. It increases slightly to 60 atoms % gold, then drops off once more.

Firth/

Firth (102) has studied the oxidation of methane on supported palladium-gold alloys. In this case the apparent activation energy was greatest on gold, fell to 60 at.% gold, and then remained constant for the rest of the series. This was also true for the oxidation of ethylene on palladium-silver films (103).

Hanna (104), however has described the decomposition of hydrogen peroxide on palladium-gold alloys, for which gold shows the greatest activity and the least activation energy, fitting in well with Bowden's (101) prediction.

Gerberich et al (105) have studied the partial oxidation of ethylene on palladium-gold sponges, to give mainly carbon dioxide with up to 45% of acetic acid, acetic anhydride, acetaldehyde and ethylene oxide; palladium was the most active catalyst, with a secondary peak of activity at around 20 atoms % palladium, this secondary peak also coincided with the maximum selectivity. They suggested that complete oxidation was related to the ability of the catalyst to dehydrogenate the ethylene, hence the high selectivity of low palladium alloys. Gold was almost totally inactive for the reaction. The authors suggest furthermore that the active sites on the surface are palladium atoms or clusters of atoms. This statement is supported by carbon monoxide adsorption measurements, combined with the equation of Brennan et al (106) of the number of surface atoms, and, hence, of palladium atoms.

In conclusion, then, it must be said that the evidence is confused, for hydrogen reactions, some d-band vacancy seems to lower the apparent activation energy, and it may be that Fermi level is important, while for oxygen/

oxygen reactions the facts seem to be contradictory if a unified theory of catalytic activity is to be considered. It is essential, then, that more information be gathered on reaction mechanisms. Ultimately, of course, the bulk properties of the alloys, both geometric and electronic, depend upon the structures of the individual constituent atoms and the question is "How are the properties of the surface atoms related to the bulk properties of the metal?" The related question "How are the properties of the surface atoms affected by a chemisorbed layer?" must also be asked. The answers to neither of these questions, in the present state of knowledge, are known, but it would seem to be dangerous to assume to direct a relationship between the properties of the alloy, in the bulk state, and the properties of an almost isolated surface atom, which is chemically combined with, say, a methyl radical, or a formate ion.

CHAPTER 2.

EXPERIMENTAL

2.1 Apparatus:

The reactions were carried out using a fairly standard high vacuum gas line, as illustrated, which was constructed of pyrex glass and in that part which was used for handling the dimethyl acetylene (which is highly soluble in most tap greases), fitted with greaseless high vacuum taps, of either the type supplied by "West Glass" of California or by "J.Young" of Acton which were capable of maintaining the necessary high vacuum.

The reaction vessels were all 0.15 l in volume and were fitted with "West Glass" greaseless joints which utilise viton O-rings.

The reaction was monitored by removing samples from the reaction vessel at intervals, dictated usually by the retention time of the chromatography column; and passing them, by means of a nylon tube and a Perkin-Elmer Gas Sampling Valve, into a Perkin-Elmer F II gas-liquid chromatograph, with a single head, flame ionisation detector (107). The four metre column was packed with a 20:50 mixture of bis-2-methoxy ethyl adipate adsorbed on 60 - 80 mesh Chromosorb P, (see below).

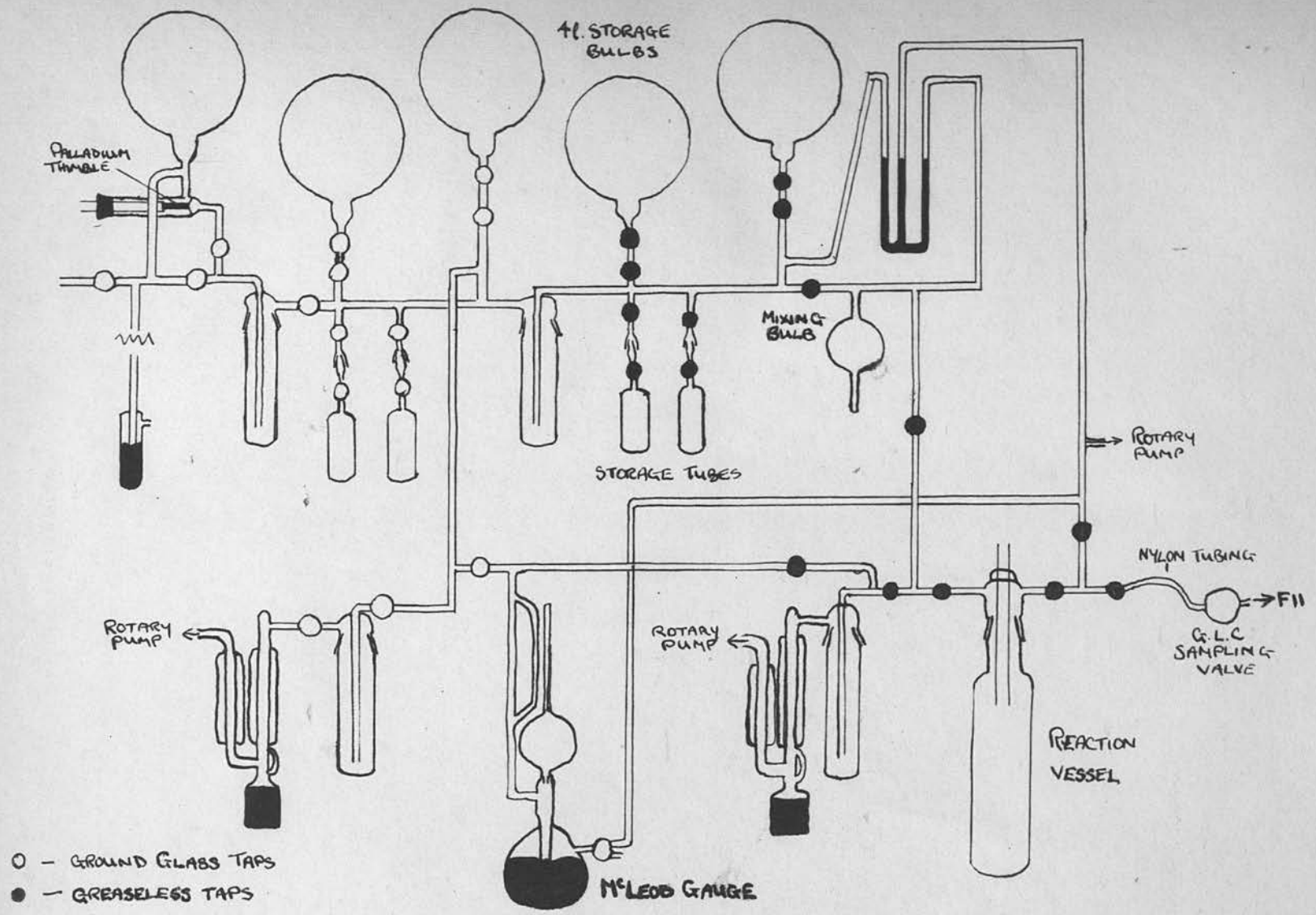
The relative peak sizes, as indicated by the ionisation amplifier, were measured by a Kent Chromalog electronic integrator (108) and were also recorded by a Sunvic Type 105 pen recorder, connected to the output of the Chromalog.

2.2 Chemicals:

The chemicals used, apart from the catalysts, were few

i) Dimethyl acetylene (but-2-yne):

As/



DIAGRAMATIC REPRESENTATION OF THE GAS LINE

Fig1

WATER-COOLED JOINT

(For the Reaction Vessel)

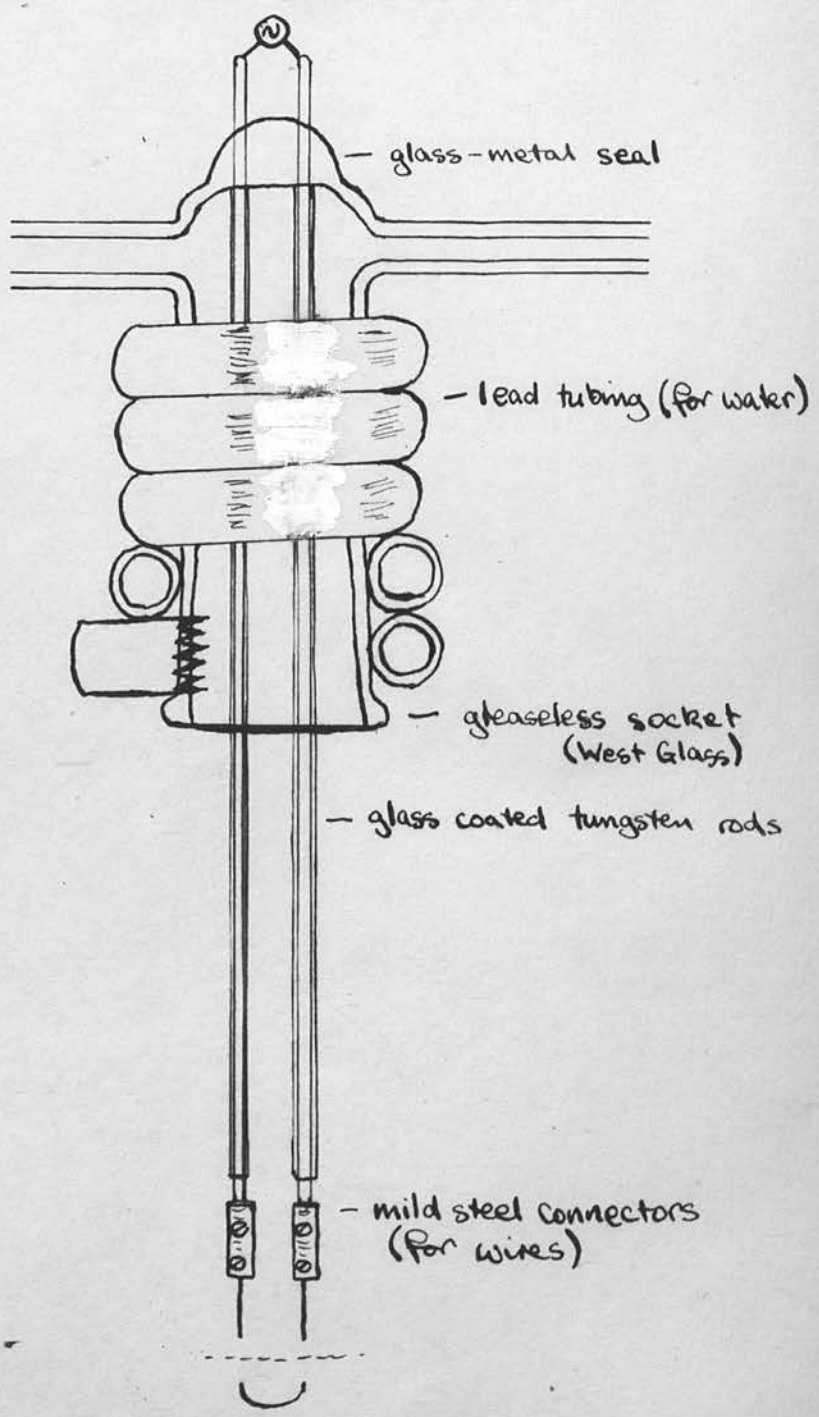


Fig2

As supplied by Cambrian Chemicals Ltd., (b.pt 27°C) after several distillations in the gas line, with rejection of top and bottom sections, the compound was usually approximately 99.85% pure: and the major impurity was ethyl acetylene (but-1-yne) usually 0.12% and the remaining 0.03% or so was formed of butenes, butane and methyl acetylene. A sample of high purity dimethyl acetylene was prepared by using a preparative gas-liquid chromatograph. This sample was found to be 99.99% pure, as analysed by the F II, its activity in catalytic reactions in no way appeared to be different to the normal chemical, which was generally used for the reactions.

ii) Hydrogen:

This was prepared by diffusion of cylinder hydrogen (BOC) through a palladium/silver alloy thimble, as supplied by Johnson Matthey Metals Ltd. and stored in a five litre bulb attached to the apparatus.

iii) Oxygen:

Cylinder oxygen (B.O,C.) was stored in a five litre bulb, and used directly.

2.3 The Catalysts:

The catalysts used were either supplied directly by Johnson-Matthey or were prepared by materials supplied by Johnson-Matthey utilising tungsten wire supplied by the "Tungsten Manufacturing Co.(1958) Ltd".

The palladium-gold catalysts, the 0.2 mm. diam. palladium wire and all the/

the gold wires used were Johnson-Matthey "specpure" quality; i.e. impurities total less than 10 parts per million.

The palladium wire of 0.28 mm. thickness was Grade I, that is total impurities were less than 60 p.p.m.

2.4 Gas-Liquid Chromatography

An outline of the theory of gas-liquid chromatography is included in the instruction manuals of most commercial G.L.C.'s (107) but several books have been written which give a more detailed description (109,110). Briefly, however, the system depends upon a column containing a porous solid on which is adsorbed a liquid or near liquid. The sample of gases to be analysed is passed into the column in a stream of inert carrier gas and is dissolved in, or adsorbed on, the liquid phase from which it will also be extracted by the carrier gas. Obviously, the rate at which these two steps occur depends upon the affinity of each particular gas for the liquid phase. So, in effect, a continuous partitioning takes place down the column provided the affinities of the gases differ. If the materials and conditions are chosen correctly then, when the end of the column is reached, the gases will have been separated.

The great difficulty lies often, in finding a column suitable for the mixture of gases to be analysed. In the present work this was not particularly easy since a column was needed which would separate butane, the straight chain butenes and 2-butyne. Unfortunately acetylenes tend to be much more soluble than the corresponding olefins and paraffins while, to separate isomeric olefins, a column is needed which has a fairly high affinity for hydrocarbons; i.e. it will have a high retention time for acetylenes. The/

The column which was eventually chosen was, as stated, a 20:80 ratio mixture of bis-2-methoxy ethyl adipate and chromosorb P packed into a four metre column. This particular column is designed for use between room temperature and 100°C for the separation of light hydrocarbons. Unfortunately the retention time for dimethyl acetylene was eighteen to twenty minutes: the butenes were adequately separated, however, between four and a half and seven minutes, thus it was possible to run overlapping samples.

The operating temperature was 35°C. Although this did not give perfect separation of cis-and trans-but-2-ene the possible error was small. If the temperature was reduced to improve the separation, then the retention time of the dimethyl acetylene increased markedly.

The detector used for the gases in this case, was of the flame ionisation type, which are linear in their response to within close limits. Their sensitivity to chemically different carbon atoms does vary, however, so the sensitivity of the F II detector was determined for some of the gases which it may be expected would occur during analyses.

Four gases were compared by admitting mixtures of two of the gases, both at one cm. pressure of mercury, to the reaction vessel. Samples were then abstracted from the gases, analysed by the G.L.C. and the peak sizes compared.

The four gases tested were:

	Sensitivity (rel. to Butane)
i) Butane	1
ii) trans-but-2-ene	0.98

iii)/

		Sensitivity (rel. to butane)
iii)	cis-but-2-ene	0.99
iv)	but-2-yne	1.09

2.5 Calibration of Apparatus:

i) Thermocouple (for reaction vessel temperature)

A chromel (T_1)/alumel (T_2) thermocouple, for use in the reaction vessel sand bath was prepared and checked using a platinum resistance thermometer. The results obtained agreed closely with literature (III) values over a wide range of temperatures, i.e. 22°C - 416°C.

ii) Apparatus Volumes.

All reaction vessels were manufactured to be 0.150 ± 0.001 l. in volume.

The remaining volumes in the gas line, whose sizes were of interest, were measured by the method of hydrogen expansion, from a bulb of known volume. The values found, were

a) ancillary tubing before mixing volume

0.072 l.

b) mixing volume

0.403 l.

c) connecting tubes

0.009 l.

d) reaction vessel, and volume above joint

0,175 l.

∴ volume above joint = 0.025 l.

2.6/

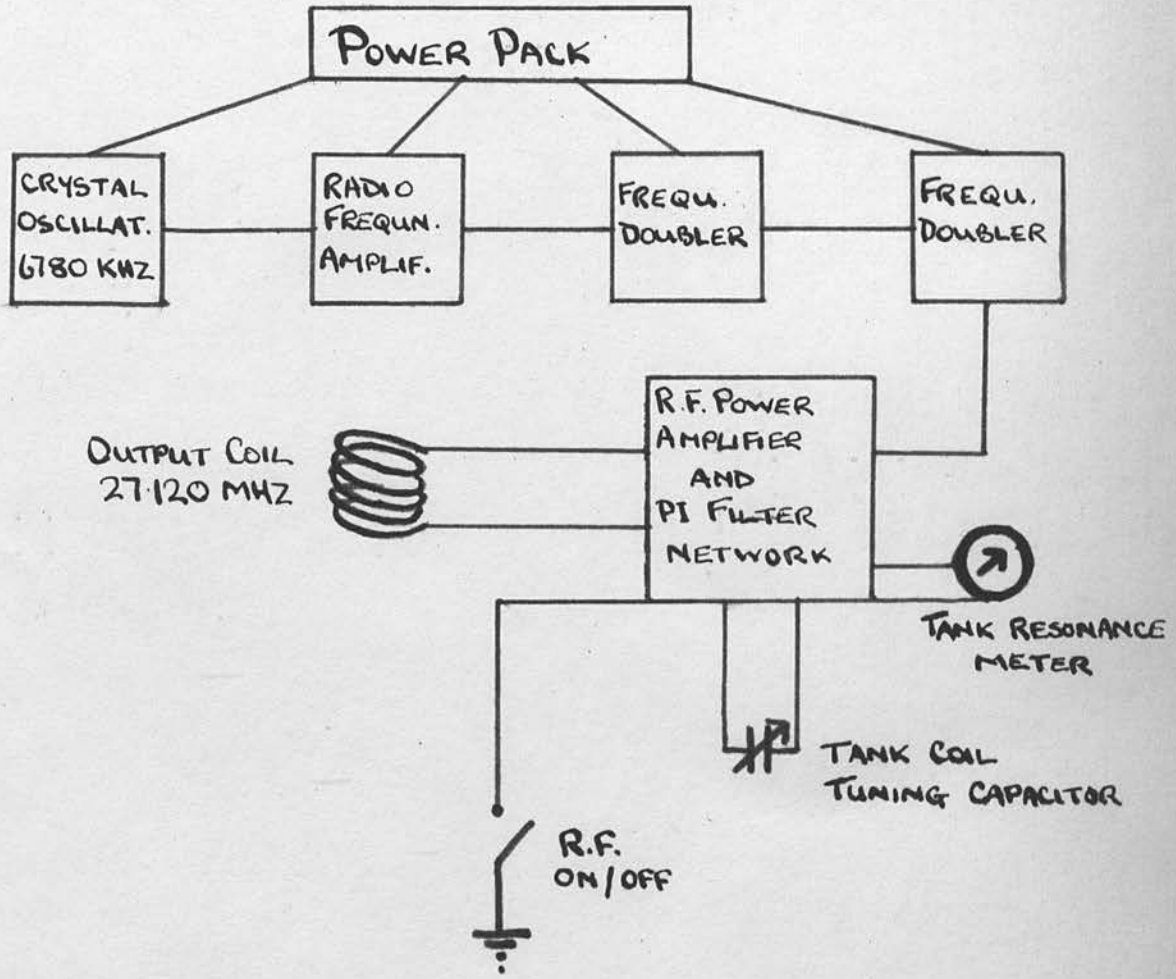
2.6 Radio-Frequency Generator:

The radio frequency generator, used in work on wire catalysts, had an output in the region of 100 watts, at 27.12 M.Hz and was crystal controlled; the output was pure R.F.

A small detector was also used to monitor the output, this consisted of a short aerial, connected to a diode circuit, tuned to the correct frequency. This was in turn connected to a milliammeter which recorded the output.

The generator was fitted extensively with R.F. chokes and a PI filter network to filter out all harmonics of the basic 27.12 M.Hz. which is a G.P.O. allocated frequency.

Radio Frequency Generator – Block Diagram



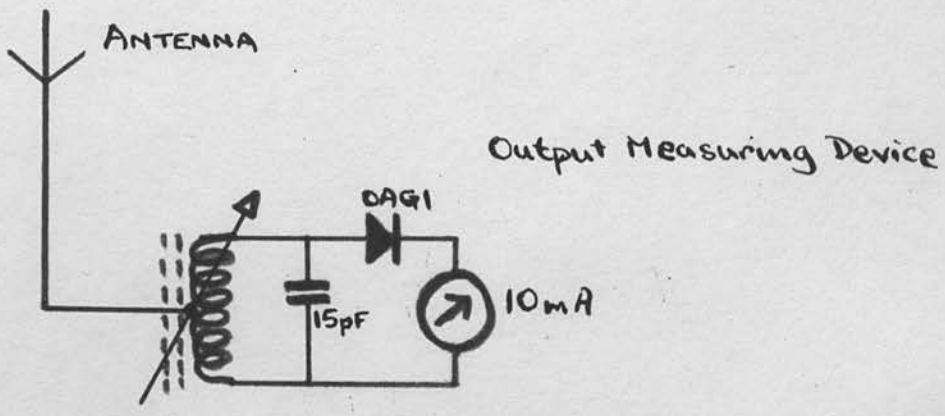


Fig 3

CHAPTER 3.

THE HYDROGENATION OF DIMETHYL ACETYLENE OVER SOME PALLADIUM CATALYSTS

3.1 Some notes on the Palladium-Hydrogen system:

The permeability of transition metals to hydrogen has been known for a long time (112). The first recorded observations on the palladium-hydrogen system were by Graham in 1866 (113), and the work done on this system, between then and 1967, has been extensively reviewed, in book form, by Lewis (114).

Palladium exhibits an unusually high permeability to hydrogen and is also able to occlude large quantities of the gas. In doing so it appears to form two distinct phases;

i) The α-phase, which occurs at lower hydrogen contents. The equilibrium pressure of hydrogen shows a continuous increase and in this region the solid can be considered as a solid solution of hydrogen in palladium lattice. Eventually, as more hydrogen is added to the system, the equilibrium pressure ceases to increase. This point, known as α_{mx}, corresponds with the maximum solubility of hydrogen in the α-phase structure; it is also the point at which a new hydride phase, the β-phase, begins to nucleate.

ii) The β-phase, after the α_{max} point has been reached, coexists with the α-phase while more hydrogen is added; the equilibrium pressure of hydrogen remains constant. When the phase transformation is complete, i.e. all the solid is in the β-phase, the equilibrium hydrogen pressure will once more increase as more hydrogen is added/

added, further occlusion of hydrogen, however, is regarded as being solution of the hydrogen in the β-phase.

The precise points at which these transitions occur vary with temperature and possibly with the sample of palladium, however the α_{max} point usually occurs in the region

$$H:Pd \simeq 0.1$$

and the point at which the solid becomes totally β-phase when

$$H:Pd \simeq 0.5$$

It is of interest to note that Everett and Nordon (115) were unable to obtain reproducible pressure/composition curves, using palladium wires, above 120°C.

As has already been mentioned, Joice et al (99) have noted unusual catalytic properties for palladium catalysts in the transition region when it would seem that surface hydrogen species must be particularly plentiful.

The kinetic stability of the palladium hydrides is rather variable and seems to depend upon the activity of the catalyst surface; Krause and Kahlenberg (116) and Hewett and Makrides (117) have both shown that massive palladium can adsorb hydrogen, almost irreversibly, in a practical sense at least (114 Chapter V.)

This has been supported by the more recent work of Sheridan and Campbell (118) on the hydrogen uptake of evaporated palladium films. They have shown that when a palladium film is thrown in an atmosphere of hydrogen, some hydrogen will be incorporated into the film and that some of this hydrogen cannot be exchanged. The amount of hydrogen incorporated in/

in the film varies with the rate of deposition and further adsorption occurs when deposition ceases. Irrespective of this about 0.6 atoms of hydrogen per atom of palladium, cannot be exchanged. This, of course, fits in remarkably well with previous comments on palladium with its 0.6 holes per atom in the d-band. It suggests some firm bonding involving the d-band (see Ch. I). Couper and Eley (85) have commented upon the poisoning effect of hydrogen for para-hydrogen conversion and have attributed this to the filling of the d-band, while Rennard and Kokes (119) have studied the hydrogen deuterium exchange on palladium hydrides and discovered that the rate of exchange depended on the composition of the hydride. This picture is only really interpretable by considering that hydrogen is bound into the lattice. Neutron diffraction measurements have shown that β-phase palladium hydride has a sodium chloride structure with only about 70% of the octahedral interstices occupied by hydrogen (120). It would be expected to be a fairly stable structure. Nace and Aston (121) inferred a structure of β-phase hydride which contained PdH_4 groups which were covalently bonded and were free to rotate. Since the most likely position for a hydrogen is between two palladium atoms this structure is not necessarily inconsistent. Sheridan and Campbell (118) also showed that at 300°K their palladium films had an adsorptive capacity of approximately 0.1 atoms of hydrogen per palladium atom.

The adsorption of hydrogen on palladium surfaces is obviously unusual, and of great interest chemically. The work of Scholten and Konvalinka (122), on the equilibration of hydrogen and deuterium, and also on the conversion of para hydrogen and orthodeuterium over palladium wires and sponges, has yielded much valuable information on the mechanism of hydrogen exchange on the/

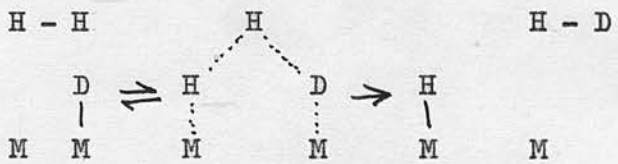
the surface of palladium and has also provided information on the effect of phase changes in the palladium hydride system. They have shown that, although changes in the surface undoubtedly occur as conditions change, and that these conditions affect the activity of the surface, they do not occur at the point at which bulk changes from α- to β-phase occur. As regards mechanism, they conclude that on α-phase hydrides, for exchange or conversion, the Bonhoeffer-Farkas mechanism operates:

i.e. dissociative chemisorption, followed by associative desorption

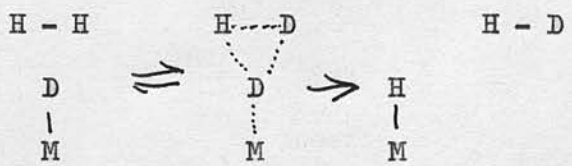
activated complex

M = metal surface site

while on β-phase hydrides, the Rideal mechanism is probably operating



as opposed to Eley's mechanism (85).



It would seem then, that three types of hydrogen may have to be considered in the palladium-hydrogen system; these are the α- and β- types and surface species, of which it is quite possible that there is more than one type. For instance, there must be physically adsorbed hydrogen/

hydrogen molecules and possibly several types of surface hydrogen atoms. There may be a chemisorbed type, as indicated in the mechanisms illustrated above, and also hydrogen atoms approximating more to the bulk species of the α- and β- phases. These may exist in "holes" in the surface lattice, such as gaps between palladium atoms, holes due to lattice faults, or holes which the hydrogen makes for itself. The system is complex and difficult one to study, but of great interest to the catalytic chemist.

3.2 The Hydrogenation of Dimethyl Acetylene on Palladium Films

3.2a The deposition of palladium films:

The films were thrown using the method described by Anderson (123), in which 0.3 m. of "spec pure" palladium wire 0.0002 m. in diameter, was wound onto 0.15 m. of 0.0003 m. diameter tungsten wire which was then weighed. The wires were then mounted in the reaction vessel and baked out overnight at 450°C. The following day, they were degassed by passing a current of 4.8A through them for thirty minutes, the reaction vessel being pumped down simultaneously. The reaction vessel was then immersed in ice and the current was raised to 6.2A; a film was deposited in ten minutes, whose weight lay between 1.0 and 1.2 ~~and~~ times 10^{-5} kg. This was determined by weighing the wires again when the reaction was completed.

The films thus produced seemed to be of a standard weight and activity, showing no tendency to flake from the reaction vessel walls and were, to the unaided eye, equal in geometric area.

3.2b/

3.2b Experimental Notes and Results:

i) An exploratory reaction was run at 0°C on a palladium film as described above

initial wt. of W/Pd. wires = 0.3224 gms.

final wt. of W/Pd. wires = 0.3096 gms.

∴ film weight = 1.28×10^{-5} kg.

The gas mixture was prepared so that the hydrogen-dimethyl acetylene ratio was 2.5.

In the mixing volume of the gas line

Dimethyl Acetylene (DMA)	=	1.40 cm.Hg. = 1.868×10^3 Nm^{-2}
Hydrogen	=	3.50 cm.Hg. = 4.670×10^3 Nm^{-2}
Total Pressure	=	4.90 cm.Hg. = 6.538×10^3 Nm^{-2}
Reaction Vessel Pressure	=	3.20 cm.Hg. = 4.269×10^3 Nm^{-2}
∴ Reaction Vessel Pressure of DMA	=	0.91 cm.Hg. = 1.214×10^3 Nm^{-2}
∴ Reaction Vessel Pressure of Hydrogen	=	2.30 cm.Hg. = 2.975×10^3 Nm^{-2}

Results of run at 0°C:

A sample of the gases taken after the reaction had been running for five minutes showed that all C_4 gases were then converted to butane.

This would indicate that, for any really useful study of this system, the temperature would need to be lowered by at least 40°C, i.e. to -40°C or -50°C. There arises then a complication in that the boiling point of DMA is 27°C, which means that it would be difficult to maintain all the DMA as vapour at such temperatures, in fact the vapour measure of DMA at -50°C is well below 1 cm. Hg. (1.334×10^3 Nm^{-2}).

However/

However this means that some information, using the present system may be obtained in the region of $-40^{\circ}C$.

ii) A reaction at $-42^{\circ}C$.

A reaction was carried out, as above, except that the temperature was $-42^{\circ}C$ maintained by an acetone/solid carbon dioxide bath.

Wt. of Pd/W wires, initial = 0.3249 gms.

Wt. of Pd/W wires, final = 0.3158 gms.

$\therefore$ Film weight = 0.0091 gms.

= $0.91 \times 10^{-5} k_g$.

A hydrogen to DMA mixture ratio 2.5:1 was again made up.

Reaction Vessel Pressure = 3.1 cm.Hg.

$\therefore$ Pressure of DMA = 8.9 mm.

Results:

The reaction was much slower than the previous one, but still went too quickly to be usefully monitored. The following analyses were obtained:

Time (mins)	butane	but-1-ene	t-but-2-ene	c-but-2-ene	DMA
4	0.7%	1%	-	66%	32%
12	21%	1%	48%	30%	-

i.e. the hydrogenation of DMA to butenes is proceeding at about 17% $min.^{-1}$.

It is probable that most of the but-1-ene in the first sample came from the trace of ethyl acetylene present in the DMA.

To/

To follow the reaction properly, and obtain an Arrhenius Plot, it would be necessary to go down to about $-90^{\circ}C$, at which temperature the vapour pressure of DMA is very low.

It was decided to do some experiments in which the order of admission of the reactants was changed.

iii) Reaction at $-40^{\circ}C$ - DMA admitted first:

A film was thrown, the weight of which was $1.10 \times 10^{-5} k_g$.

A pressure of approximately 1 cm. Hg. ($1.33 \times 10^{3} Nm^{2}$) of DMA was admitted, at $-40^{\circ}C$.

After three minutes approximately 2.5 cm. Hg. ($3.33 \times 10^{3} Nm^{2}$) of hydrogen were admitted.

Results:

After five minutes a sample of the gases contained 80% c-but-2-ene and 20% DMA, with a trace of but-1-ene, which also probably came from the trace of ethyl acetylene in the original DMA. This result is essentially identical with that obtained when the gases were admitted premixed.

iv) Reaction at $-40^{\circ}C$, Hydrogen admitted first:

A film was thrown, the weight of which was $1.24 \times 10^{-5} k_g$.

2.5 cm. Hg. ($3.33 \times 10^{3} Nm^{2}$) pressure of hydrogen was admitted to the film at $-40^{\circ}C$ and left for three minutes.

Approximately 1 cm. Hg. ($1.33 \times 10^{3} Nm^{2}$) pressure of DMA was then admitted to the reaction vessel.

Results:/

Results:

An entirely different pattern of results was obtained, from this system, The reaction proceeded very much more slowly and while it was proceeding, the film began to flake from the reaction vessel walls.

The product pattern was essentially the same, i.e. all cis-but-2-ene.

The rate of reaction was initially rather slow, certainly less than 1% min^{-1}, but accelerated, probably due to the increasing surface area of catalyst; also possibly dehydrogenation of the catalyst was affecting the rate (see later).

v) Reaction at $0^{o}C$, Hydrogen admitted first:

A film of weight $0.95 \times 10^{-5} k_g$. was thrown.

Gases were admitted as in (iv) the only difference being that the temperature of the reaction vessel was maintained at $0^{o}C$, by an ice bath.

Results:

These were broadly the same as for (iv) except that the reaction rate was quicker. The same comments on the reaction rate apply, although the initial rate of reaction may have been approximately 5% min^{-1}. The film flaked also but tended to "fill" away from the surface in a rather fine pattern rather than fall off in large pieces as in (iv).

3.3 The Hydrogenation of Dimethyl Acetylene on Palladium Wires:

3.3a The Catalysts and their Preparation:

The question of the activation of wire catalysts will be discussed fully in Chapter V. The catalysts used in this case, however, were 0.15 m. lengths of $2.8 \times 10^{-4} m.$ diameter, Johnson-Matthey Grade I palladium wire.

A/

A fresh sample of wire was used for each experiment and this was fitted into the apparatus, as illustrated. The reaction vessel and wire were then baked out overnight at 450°C under vacuum. Subsequently the apparatus was allowed to cool down and the output coil of the radio frequency generator was placed around the reaction vessel. About one cm. Hg. of hydrogen was admitted to the reaction vessel which then, along with the output coil, was immersed in liquid nitrogen. After three minutes the generator was tuned for maximum output, at which point the radio frequency detector, previously described, registered some 3.3mA. The tap to the pump was then opened slowly and hydrogen was removed until an intense purple discharge was noted around the wire. Care was taken not to remove too much hydrogen because, if this happened, a gentle, diffuse, pink discharge, general to the whole vessel, became predominant. The output power of the generator was then reduced until the detector was reading 1.0mA. The discharge was allowed to continue at this level for ten minutes after which the liquid nitrogen bath and the coil were removed, the vessel allowed to return to room temperature and the tap to the pump opened. A current of 0.9A was then passed through the wire for 90 minutes, after which time the catalyst was considered to be ready for use. The figures and times quoted are by no means all arbitrary and are discussed fully in Chapter V.

3.3b. <u>The Experiments:</u>

Since this chapter is concerned primarily with a comparison of three types of palladium catalyst only those experiments which led to the determination of the apparent activation energy for the hydrogenation of DMA over palladium wire are discussed. The remainder are covered in Chapter V.

The/

The catalysts were prepared as described above, and the reaction vessels were immersed either in solid carbon dioxide cooled acetone, or in ice-cooled water, at the desired temperature. The reaction mixture of gases was then admitted at the reaction temperature. This means that, in fact, for an identical mixture of gases in the mixing volume, slightly different reaction vessel pressures would be obtained. Owing to the high activity of the wires it was difficult to overcome this problem. It is a minor one, however, since the variation over the range of temperatures was less than 3%.

The gas mixture used was always as follows:

DMA	1.4 cm. Hg.
H_2	3.5 cm. Hg.
Total	4.9 cm. Hg.

The reaction vessel pressure was 3.3 ± 0.1 cm. Hg.

The gases were allowed into the reaction vessel, at reaction temperature and were sampled after five minutes, then at twelve minutes and thereafter at convenient intervals.

3.3c The Results:

The reaction appears to have a "warm up" period, during which it proceeds rather slowly; it then accerates and thereafter appears to be zero order until no DMA remains. The products initially are over 90% cis-but-2-ene and, if product but-1-ene is attributed to the ethyl acetylene impurity, then the product is over 98% cis-but-2-ene.

The ethyl acetylene impurity appears to hydrogenate much more quickly than the DMA, possibly it is adsorbed preferentially by the catalyst.

After/

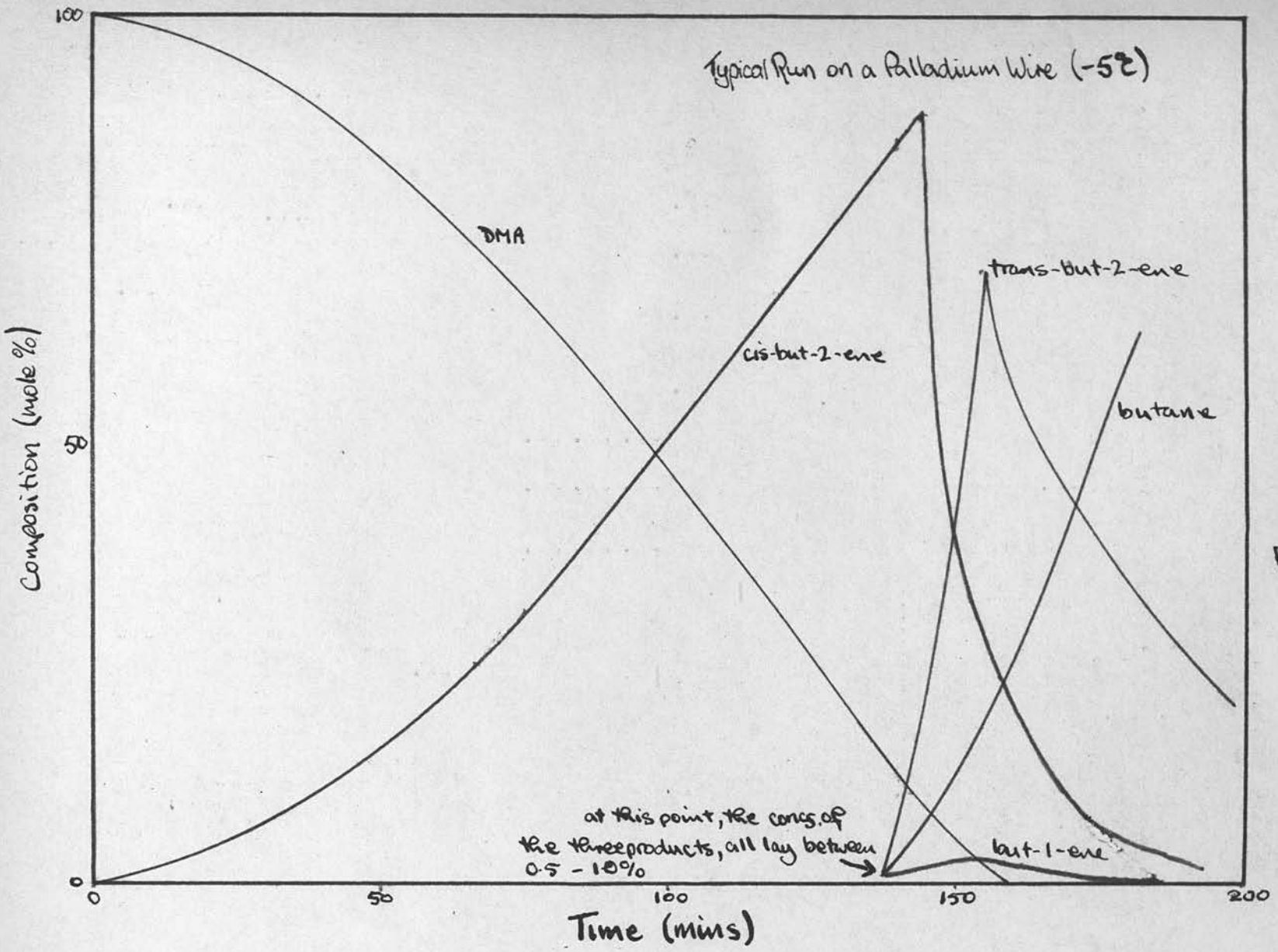

Typical Run on a Palladium Wire (-5°C)
DMA
cis-but-2-ene
trans-but-2-ene
butane
but-1-ene
at this point, the concs. of the three products, all lay between 0.5 - 10%
Composition (mole %)
Time (mins)
0
50
100
150
200

Fig 4

After all the DMA has been hydrogenated the butenes thus formed, isomerise to their thermodynamically stable ratios, fairly rapidly. This is accompanied by slower hydrogenation to butane (124).

The period of zero order reaction, is the fastest part of the initial hydrogenation reaction. This being taken as the true reaction rate for that temperature, all calculations were made using this value.

Temp. ^{o}C	Temp. ^{o}A	$\frac{1}{T}\ ^{o}A^{-1} \times 10^{-3}$	Rate $\%min^{-1}$	Log_{10} rate	Cis/Trans
-10	263	3.802	-0.64	$\bar{1}$.8062	254
-5	268	3.731	-0.88	$\bar{1}$.9445	171
0	273	3.661	-1.65	0.2175	107
5	278	3.597	-2.78	0.4440	262
10	283	3.534	-3.68	0.5680	189

The cis/trans ratio is rather uneven here. This is probably due to baseline and cut-off level fluctuations in the integrator which, although small at ratios of this magnitude, will make considerable differences. The lower values are more likely to be correct if the above assumption is correct.

The Arrhenius Plot then indicates that for an 0.15 m. length of 2.8×10^{-4}m. diameter palladium wire, activated as described, the apparent activation energy for the hydrogenation of DMA to butenes between $-10^{o}C$ and $+10^{o}C$ is 13.3 k.cals/mole.

Arrhenius'/

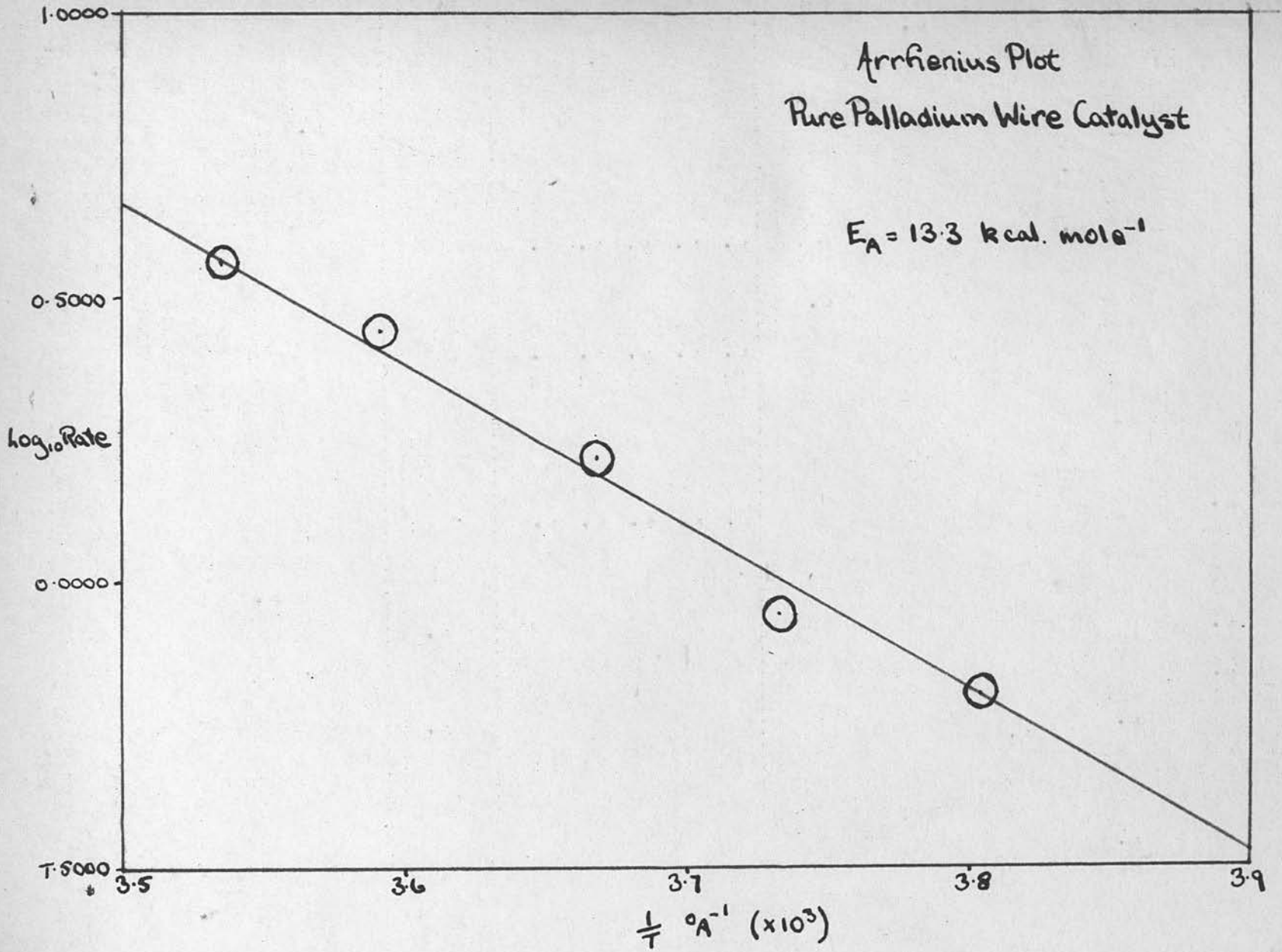

Arrhenius Plot
Pure Palladium Wire Catalyst
E_A = 13·3 k cal. mole^{-1}
1·0000
0·5000
0·0000
T·5000
$\log_{10}$ Rate
3·5
3·6
3·7
3·8
3·9
$\frac{1}{T}$ °A^{-1} (×10^3)

Fig 5

Arrhenius' gradient =

$$\frac{1.42}{0.50} = -\frac{E_A}{R \times 2.303}$$

$$\therefore E_A = 13.3 \pm 0.3 \text{ k.cal.mole}^{-1}$$

$$\therefore \text{ Apparent Activation Energy} = 55.8 \pm 1.3 \text{ k.j.mole}^{-1}$$

3.4 The Hydrogenation of Dimethyl Acetylene on Expanded Palladium Foil

3.4a The Catalyst and its Preparation:

A piece of expanded palladium foil, of mass 0.0345 k_g., was obtained from Johnson-Matthey, rolled up, and placed in a reaction vessel.

Initially, an attempt was made to activate the catalyst in a manner analgous to that used for palladium wires. This was found to be impossible, as no satisfactory discharge could be obtained. This was probably due to the speed with which small pressures of hydrogen could be adsorbed by such a large bulk of palladium. At liquid nitrogen temperatures, palladium will adsorb very considerable quantities of hydrogen.

When the foil was simply degassed overnight, at 450°C, it was found to be weakly active at 150°C. When the gauze was degassed again it was found to have lost most of its original activity, indicating that DMA hydrogenation is self poisoning on palladium foil at 150°C.

A third technique was tried in which the temperature of the reaction vessel and the foil were raised to 450°C under vacuum. A reaction vessel pressure of 5 cm. Hg. hydrogen was then admitted, and the system was left for 30 minutes, after which the hydrogen was pumped away and the foil was degassed/

degassed, overnight at 450°C. After one or two "running in" experiments, it was found that the activity of the catalyst was fairly reproducible by this method.

3.4b The Experiments:

In all, some thirteen experiments were carried out on the palladium gauze, the final seven of these being used for an Arrhenius Plot.

These seven experimental runs were all carried out in an identical fashion. The catalyst was activated as described in 3.4a. The baking-out oven was then removed and replaced by an electrically heated air/sand bath at the reaction temperature. The "standard" reaction mixture, as described below, was then made up and admitted to the reaction vessel at the reaction temperature. Again, this lead to small variations in the reaction vessel gas pressure but these were very small over the temperature range used, i.e. 89°C to 126°C.

In the mixing volume

DMA = 1.4 cm. Hg.

H_2 = 3.5 cm. Hg.

Total = 4.9 cm. Hg.

All the reaction vessel pressures lay between 3.3 and 3.4 cms. Hg. indicating that the pressure of DMA in the reaction vessel is 0.96 ± 0.01 cm. Hg.

Reaction were carried out at 89, 98, 104, 114, 115, 123, 126°C.

3.4c/

3.4c The Results:

From the previous work, it would be expected that the reaction would be zero order under the present conditions. In fact, after a short "warming up" period of two or three minutes, the reaction starts off in a manner very reminiscent of palladium wires. After a period of between ten and fifty minutes, depending on temperature, the reaction begins to show distinct signs of self-poisoning, and in no case was the complete reaction of DMA achieved.

The products were primarily composed of cis-but-2-ene, but in this case, appreciable amounts of trans-but-2-ene and but-1-ene were also obtained, along with a trace of butane. This would be expected on purely thermodynamic grounds. The cis/trans ratio of the but-2-ene products shows, as might be expected, a gradual decrease as the temperature rises; the points are not very regular, however. It is worth noting though that the most abberent points on the Arrhenius' Plot are also the most irregular on the cis/trans vs temperature plot. This may be due to differences in the state of hydrogenation of the palladium catalyst, Joice et al (99) have noted variation of product ratio with change in phase of palladium hydride catalyst for the hydrogenation of 1,3 butadiene. Hydrogen is also known to be a poison for palladium catalysts (85).

Arrhenius' plots were prepared for the disappearance of DMA and for the formation of cis- and trans-butenes. The quantities of but-1-ene and of butane produced were insufficient for meaningful calculations to be made although the results were consistent.

All calculations were made using the fastest rate measured during the reaction.

i)/

Temp ^{o}C	Temp ^{o}A	$\frac{1}{T}\ {}^{o}A^{-1} \times 10^{-3}$	DMA Reaction rate $\%min^{-1}$	Log_{10} Rate (DMA)	cis-but-2-ene Reaction rate $\%min^{-1}$	Log_{10} Rate (C-but-2-ene)	t-but-2-ene Reaction rate $\%min^{-1}$	Log_{10} Rate ($_{t\text{-but-2-ene}}$)
89	362	2.762	-0.1376	$\bar{1}.1387$	0.1212	$\bar{1}.9835$	0.018	$\bar{2}.2553$
98	371	2.695	-0.6250	$\bar{1}.7959$	0.5091	$\bar{1}.7068$	0.056	$\bar{2}.7482$
104	377	2.653	-0.5172	$\bar{1}.7137$	0.4511	$\bar{1}.6543$	0.073	$\bar{2}.8633$
114	387	2.584	-1.731	0.2382	1.625	0.2108	0.196	$\bar{1}.2923$
115	388	2.577	-1.379	0.1397	1.030	0.0128	0.138	$\bar{1}.1399$
123	396	2.525	-1.720	0.2356	1.557	0.1923	0.250	$\bar{1}.3979$
126	399	2.506	-2.333	0.3680	1.648	0.2169	0.325	$\bar{1}.5119$

i) Reaction of DMA

$$\text{gradient} = \frac{-1.40}{0.302 \times 10^{-3}} = \frac{E_A}{R \times 2.303}$$

$$\therefore E_A = 20.8 \pm 0.4 \text{ k.cal. mole}^{-1}$$

$$= 87.4 \pm 1.7 \text{ k.j. mole}^{-1}$$

ii) Formation of cis-but-2-ene

$$\text{gradient} = \frac{-1.383}{0.265 \times 10^{-3}} = \frac{E_A}{R \times 2.303}$$

$$\therefore E_A = 20.5 \pm 0.5 \text{ k. cal. mole}^{-1}$$

$$= 86.1 \pm 2.1 \text{ k.j. mole}^{-1}$$

iii) Formation of trans-but-2-ene

$$\text{gradient} = \frac{-1.55}{0.333 \times 10^{-3}} = \frac{EA}{R \times 2.303}$$

$$\therefore E_A = 21.5 \pm 0.9 \text{ k. cal. mole}^{-1}$$

$$= 90.3 \pm 3.8 \text{ k.j. mole}^{-1}$$

This is as expected, the activation energy for the formation of trans-but-2-ene being slightly higher than that for cis-but-2-ene.

Selectivity:

As previously mentioned, the selectivity of the reaction for the production of cis-but-2-ene is still very high. The degree of selectivity will be expressed in terms of S,

$$\text{where } S = \frac{\text{conc. of cis-but-2-ene}}{\text{Total conc. of all butenes and butane.}}$$

The ratio of the cis and trans-but-2-enes is also an interesting figure with relation to selectivity.

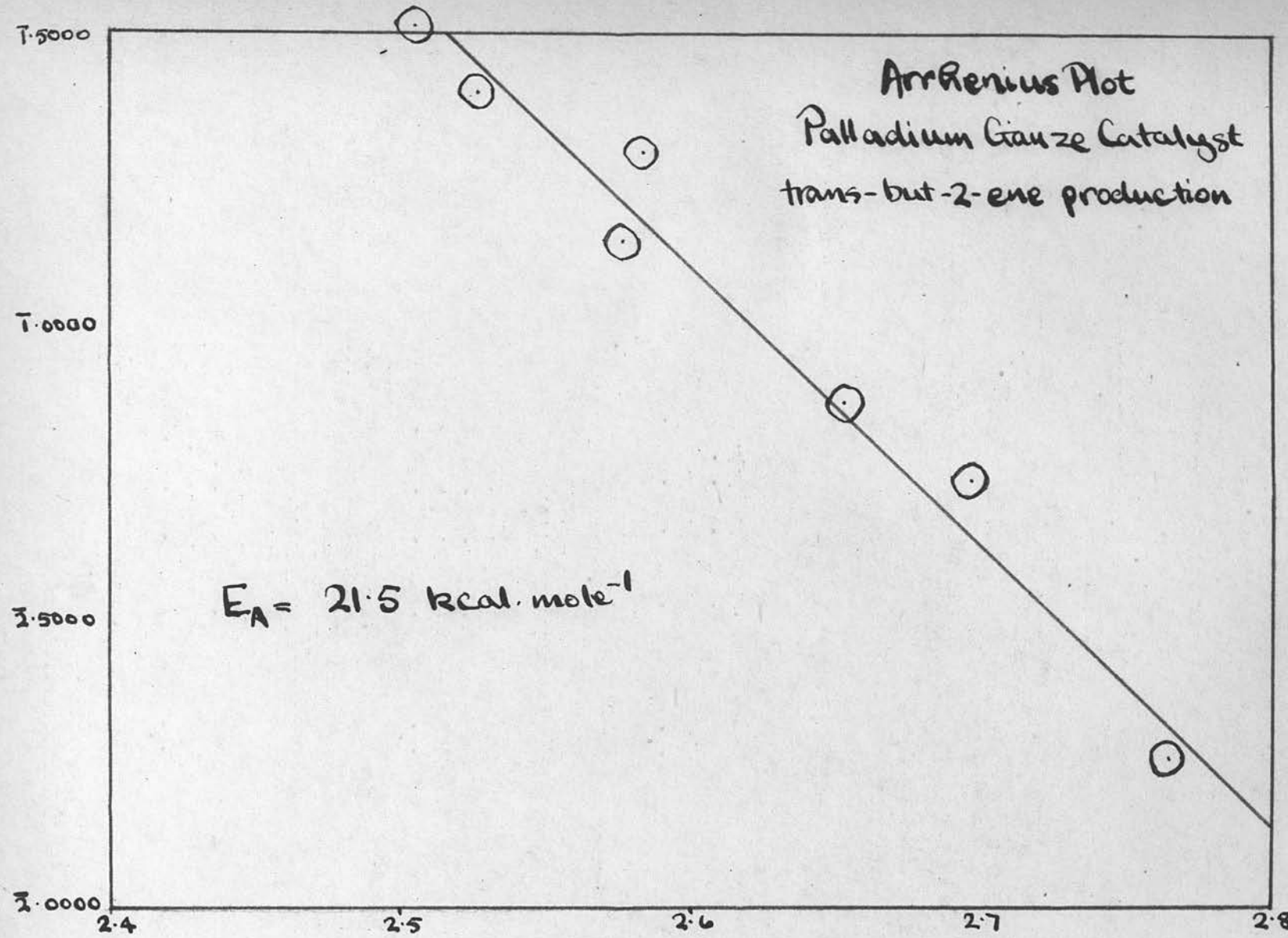

Arrhenius Plot
Palladium Gauze Catalyst
trans-but-2-ene production
E_A = 21·5 kcal. mole^{-1}
1·5000
1·0000
1̄·5000
1̄·0000
2·4
2·5
2·6
2·7
2·8

Fig 6

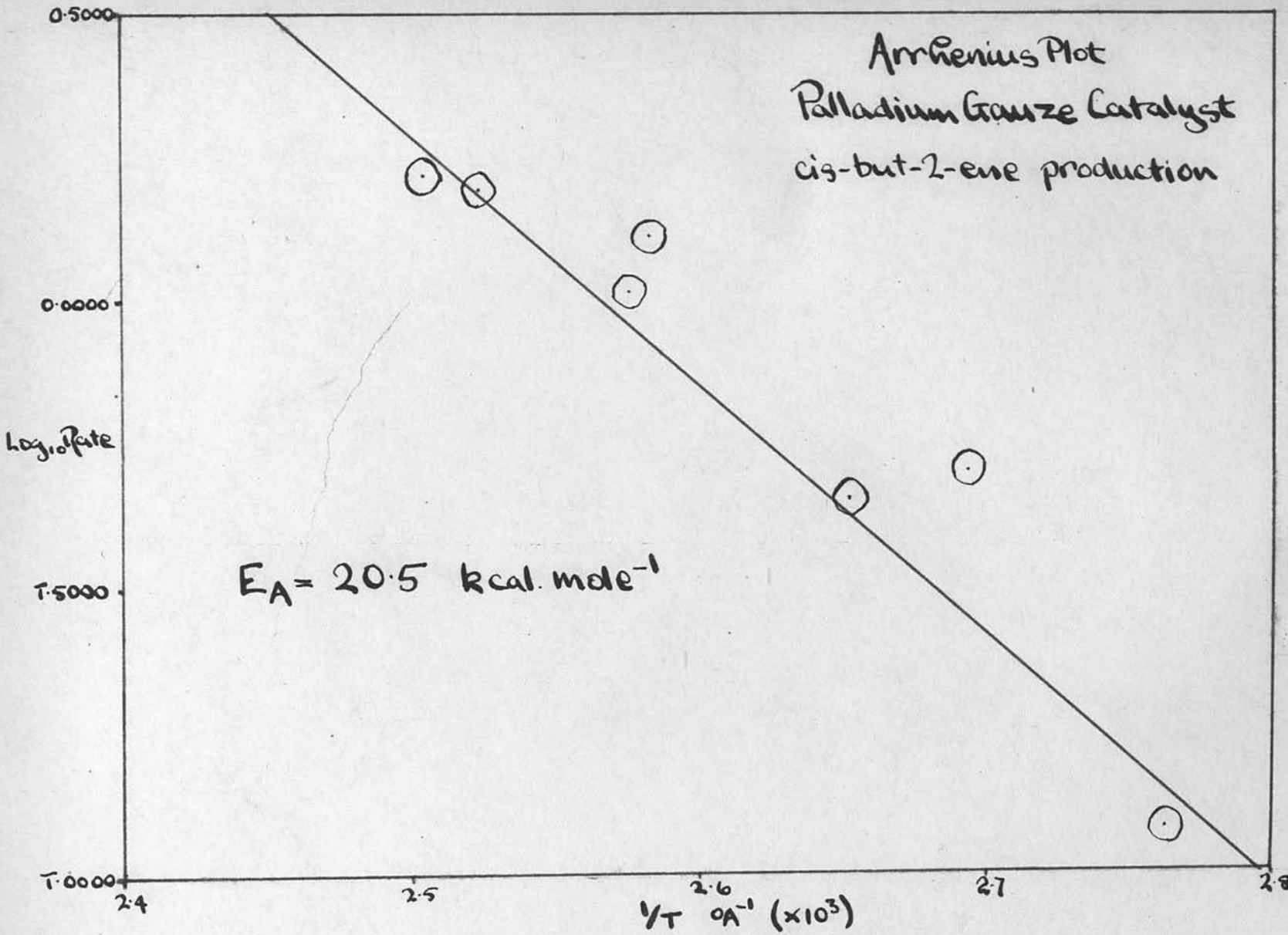

Arrhenius Plot
Palladium Gauze Catalyst
cis-but-2-ene production
$E_A = 20.5$ kcal. mole^{-1}
0·5000
0·0000
T·5000
T·0000
Log$_{10}$Rate
2·4
2·5
2·6
2·7
2·8
1/T °A^{-1} (×10^3)

Fig 7

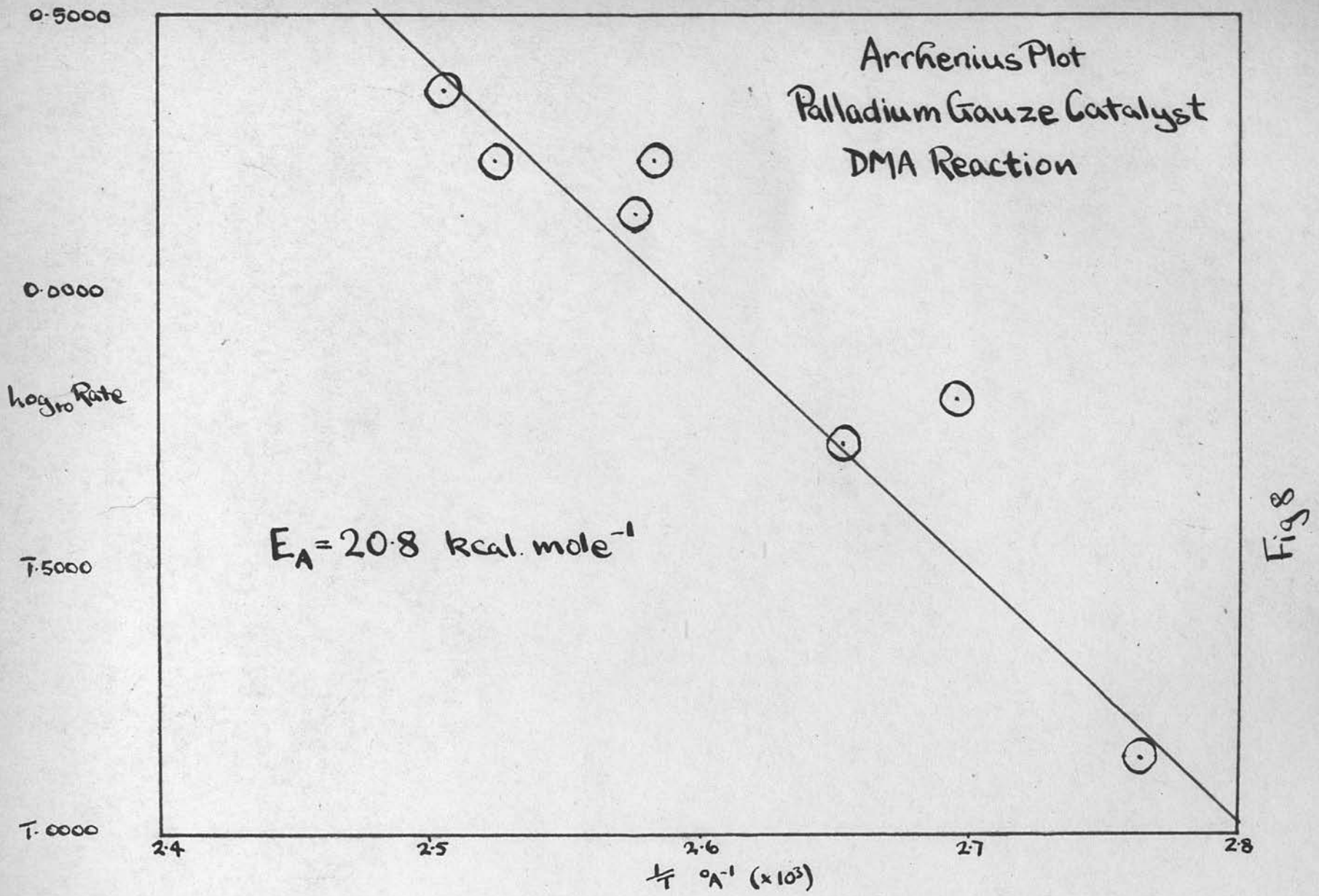

Arrhenius Plot
Palladium Gauze Catalyst
DMA Reaction
$E_A = 20.8$ kcal. mole^{-1}
0·5000
0·0000
T·5000
T·0000
log$_{10}$ Rate
2·4
2·5
2·6
2·7
2·8
$\frac{1}{T}$ °A^{-1} (x10^3)

Fig 8

Temp °C	cis/trans	S
89	6.73	0.848
98	9.09	0.883
104	6.18	0.837
114	7.02	0.860
115	7.46	0.856
123	6.23	0.827
126	5.07	0.796

These figures are rather interesting in that while both show a tendency to decrease as the temperature increases, an effect which would be expected, the cis/trans ratio is very uneven. The values of S, though not totally consistent, are much more so, suggesting that the catalyst may tend in some cases to favour the production of but-1-ene as opposed to trans-but-2-ene as a minor product, or that the catalyst was unusually selective for cis-but-2-ene.

In fact, the runs at 89°C and 115°C were more active than might have been expected by comparison with the other results, for both cis and trans-but-2-ene production, but particularly for the cis isomer: hence the high values for cis/trans and S. It is tempting to think that this may be due to the catalyst being especially free of hydrogen in these cases.

3.5/

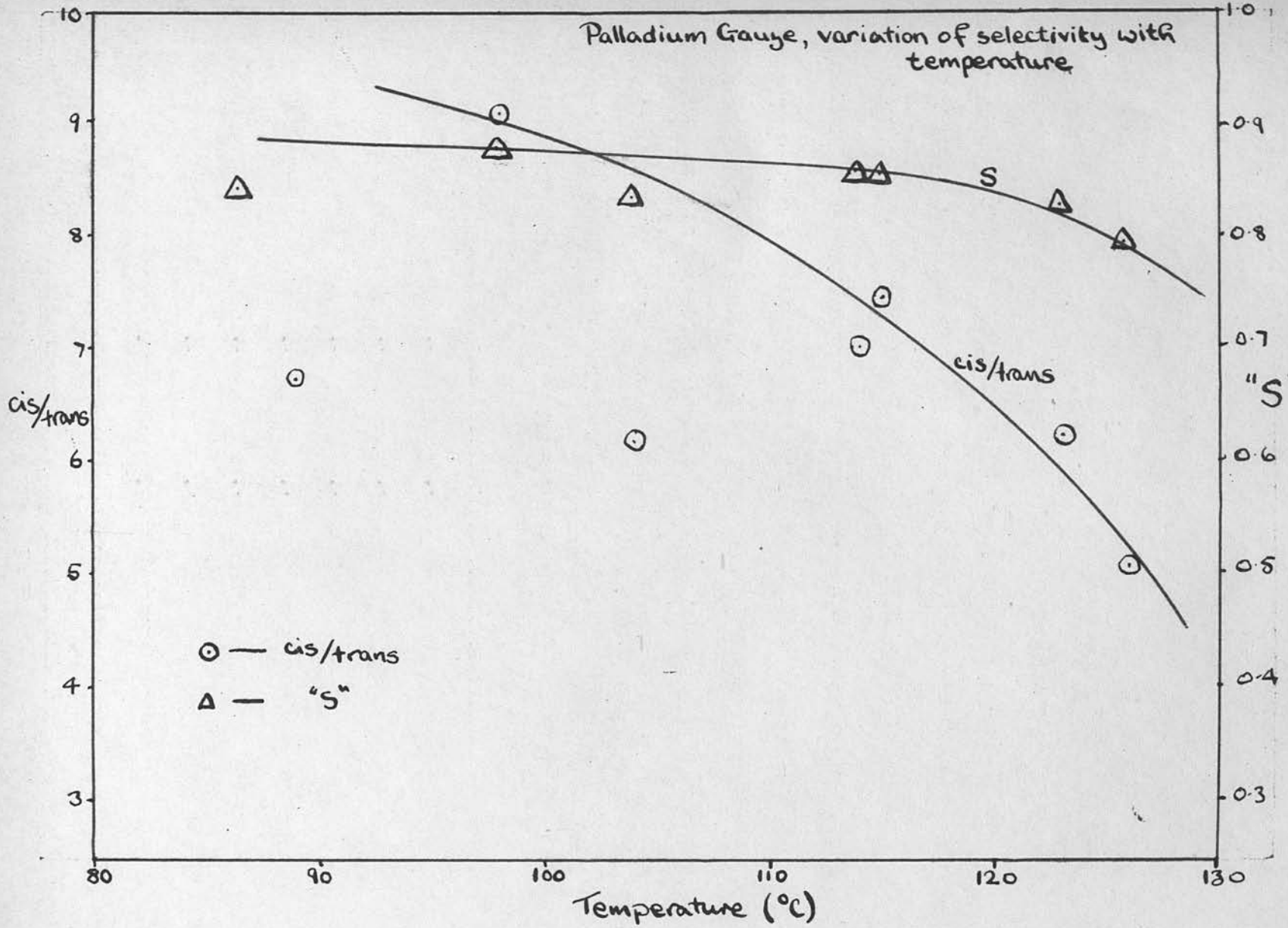

Palladium Gauge, variation of selectivity with temperature
cis/trans
"S"
S
cis/trans
⊙ — cis/trans
Δ — "S"
Temperature (°C)
10
9
8
7
6
5
4
3
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
80
90
100
110
120
130

Fig 9

3.5 Discussion:

Undoubtedly, the two main points which arise from this work are

i) The enormous difference in the catalytic activities of the three catalysts.

ii) The effect of absorbed hydrogen on the reaction rate.

The gap in activities between palladium film and palladium wires was to be expected. The very clean, unannealed surface of the film would almost certainly have a large active surface. On the other hand, the wires with only a small fraction of the surface area, cleaned only by hydrogen atom bombardment, and annealed for 90 minutes by a current of 0.9A could hardly rival this activity.

The geometric ratio of the surface areas is in the region of 100:1 in favour of the film and any "roughness" coefficient would almost certainly favour the film. If it is assumed, in fact, that the apparent activation energies and roughness coefficients are approximately equal then the difference in reaction temperature, of approximately $60^{o}C$, for equal rates, is about correct.

It is perhaps surprising that the expanded foil catalyst is so inactive. Of course, given the activation procedure employed, it is unlikely that it could possibly approach the activity of the wire catalysts. Considering however, the surface area of the foil, geometrically in the region of 0.09 m^2 in comparison to the wires geometric area, $1.3 \times 10^{-4} m^2$, the difference is very large, indicating a staggering difference in surface activity. The ratio of the frequency factors is over 10^3. This is a large difference, and difficult to explain solely in terms of differences in activation procedures.

The/

The results for palladium film indicate that hydrogen is able to poison the catalysts very effectively for this reaction, so it would seem that palladium hydrides are relatively poor catalysts for the reaction. It is already known that massive palladium can retain hydrogen almost irreversibly (116) so it may well be possible that the palladium foil retains enough hydrogen to poison its reaction a little.

It is also of interest to note that the DMA must effectively prevent hydrogen being occluded by the palladium. Probably the DMA is adsorbed on the more active surface sites, which would otherwise be very active for atomising the hydrogen molecules, prior to adsorption. Hydrogen will then only be adsorbed on less active sites lying between the bulky DMA molecules, and perhaps at such a rate it is almost all abstracted immediately by the DMA during the hydrogenation process.

One conclusion of this work is that, when palladium catalysts are being used in conjunction with hydrogen, great care must be taken to specify the conditions under which the palladium and hydrogen interact. It is common practice to activate supported palladium catalysts by hydrogen pretreatment, and it is much commented upon that the initial activity of these catalysts drops off sharply to a constant value. This could be due to some hydriding of the catalyst, which was fairly constant under the conditions of use.

CHAPTER 4

THE HYDROGENATION OF DIMETHYL ACETYLENE ON SOME GOLD CATALYSTS.

4.1 Gold Surfaces and Gold Catalysts:

The catalytic activity of gold surfaces is slightly mysterious in that there are no vacancies in the outer d-band of the bulk solids, and the outer s-band is not available for adsorption. Metals having a filled d-band are usually unable to adsorb any gas other than oxygen. The main exceptions are copper and gold, and this is attributed to the relatively low promotional energies required for excitation from the d-band to the s-band. Gold will not appreciably chemisorb hydrogen, carbon dioxide or nitrogen, while the heat of adsorption of carbon monoxide lies between values typical for physical and chemical adsorption (125). It has thus been suggested that for carbon monoxide and acetylene an unusually strong physical adsorption occurs on gold (126,p.232).

However, a more likely explanation is the one mentioned above. The d-s promotional energy required for gold is 3.25 eV (3.0 eV for copper), it is quite possible that such promotions could accompany chemisorption thus creating d-band vacancies for bonding. The d-s promotional energy for silver, which does not chemisorb acetylene, is 4.0 eV, i.e. considerably higher. The interaction between hydrogen and gold surfaces is a rather complex one. Undoubtedly, under normal conditions, gold is incapable of chemisorbing hydrogen, i.e. it cannot break the hydrogen-hydrogen bond. This does not mean that a gold-hydrogen bond cannot be formed; simply that the total energy thus available does not exceed the necessary 105 k.cal. $mole^{-1}$. It is a well established fact (127) that gold can adsorb/

adsorb hydrogen atoms if it is supplied with them, although desorption as hydrogen molecules commences at temperatures above -78°C. A number of chemists have studied the system and their evidence would indicate that more than one type of adsorption occurs. The work of Pritchard and Tompkins (128) and of Pritchard (129), into hydrogen adsorption on gold, indicates that at -183°C (90°K) hydrogen atoms on gold are immobile, with equilibrium coverages in the region of 0.2. However, it is possible to achieve greater coverages than this by supplying hydrogen atoms below -183°C. Pritchard (129) has also shown by xenon adsorption methods that a gold film thrown at -183°C, then annealed at 60°C, has a surface area twice that of a film thrown at 60°C, which has itself, a surface area twice the geometric. The hydrogen-deuterium reaction has been used by Mikorsky, Boudart and Taylor (130) to investigate surface hydrogen species. They suggested d-s promotion as the means by which the catalysts became active and suggested also, in view of the low coverages of hydrogen on gold, that an Eley-Rideal mechanism must operate which could be described as a chain reaction. Boreskov, et al have also investigated this reaction (131). Trapnell (126) has shown that the para-hydrogen conversion reaction is a good test for the chemisorption of hydrogen on metals whose adsorption is negligible. Couper et al (132) and Holden and Rossington (133) have investigated para-ortho hydrogen conversion on gold films. No pressure dependence for the conversion was observed between pressures of 2 and 20 mm. Hg and at 393 - 433°K. It may be that because of the very low coverage on gold that very low pressures would be needed before any dependence could be observed.

An/

An interesting piece of work by Yates (134) has shown that gold supported on silica will deuterate -OH groups on the silica, at near room temperatures, indicating that the gold is capable of dissociating deuterium under those conditions. The temperature must be raised to 300°K before plain silica can perform this for itself. Isothermal adsorption studies on supported catalyst showed very small amounts of hydrogen adsorption.

As might perhaps be expected, gold is not a very active catalyst and has not been greatly studied as such, apart from its role as an alloying agent in palladium-gold or silver-gold alloys. Some studies have been made, however, primarily using gold as dehydrogenation catalyst. This is entirely logical in the light of the preceeding knowledge. Erkelens, Kemball and Galwey (134), and Chambers and Boudart (135) have investigated the hydrogenation/dehydrogenation and deuteration (134) of cyclohexene.

Erkelens et al (134) found that gold films when used as hydrogenation catalysts for cyclohexene yielded mixtures of cyclohexane and benzene, the proportion of the latter increasing with temperature. The dehydrogenation reaction occurred much more efficiently than the hydrogenation. Some exchange of cyclohexene and deuterium occurred, although cyclohexane d_o was yielded as the major hydrogenated product, i.e. self hydrogenation is the important reaction. This is to be expected since the coverage of hydrogen or deuterium adsorbed from the gas phase will be small.

Chambers/

Chambers and Boudart (135) have shown that over gold powder, in the absence of hydrogen, high yields of benzene and cyclohexane are obtained and that high partial pressures of hydrogen will suppress the benzene yield. In the presence of oxygen benzene is almost the sole product.

Stoddart and Kemball (136) have shown that acetone and hydrogen over gold films yield isopropanol as the sole product, while Sachtler and Fahrenfort (137) have shown that gold will effectively dehydrogenate formic acid and, when deuterated formic acids are added, will yield a thermodynamically stable mixture of H_2, DH and D_2.

The main points which emerge, then, are that gold can break the carbon-hydrogen bond but is only marginally able to break the hydrogen-hydrogen bond on a very small number of sites. The hydrogen atoms thus evolved act almost as chain initiators in exchange reactions.

4.2 The Hydrogenation of Dimethyl Acetylene on Gold Wire:

4.2a The activation of gold wire catalysts:

In all three methods of activating gold wires were considered.

i) "Flashing": this was carried out by first baking out a wire, in position in the reaction vessel, overnight at 450°C. The wire was then electrically heated to dull red incandescence for five minutes each in first oxygen and then hydrogen, both at 1 cm. Hg. pressure. The reaction vessel was then, once more, baked out at 450°C for two hours at which time the wire was considered to be activated.

ii) Bombardment of the wire with hydrogen atoms, as described in Chapter 3, for the activation of palladium wires:

iii)/

iii) For wires which seemed to have become deactivated in use, an attempt was made to revive their activity by flaming them in air with a coal gas/oxygen flame, followed by treatment as described in (i).

Generally speaking, the method described in (1) was utilised. It was generally found that a wire, once activated by this technique, would give a number of fairly reproducible experimental runs, with intermediate reactivation and degassing. Always, however, the wire was eventually strongly deactivated and attempts to reactivate such a wire, rarely succeeded. On some occasions this was undoubtedly due to traces of mercury reaching the reaction vessel; even flaming in air would not revive the wire when this had occurred. Usually, though, the poisoning appeared to be connected with the reaction, i.e. self-poisoning. This may have been due to either strongly adsorbed acetylenic species blocking the surface, or possibly to polymer molecules on the surface. In any case it was often not possible to fully reactivate the catalyst. Experiments carried out at temperatures below 350^{o}C, required the catalyst to be reactivated as in (i) between runs. Above 350^{o}C several runs could often be carried out between reactivations without any great change in the reaction pattern being noticed.

On balance it seems possible that carbon species built up on the active sites of the catalyst and that these were not always easily burnt off by the oxygen.

4.2b/

4.2b Experiments with gold wires:

All experiments were carried out using 0.15 m. lengths of "specpure" gold wire, 2.8×10^{-4} m. in diameter. These were activated as described in 4.1 (i) and a gas mixture, as described below, was admitted at reaction temperature.

The following gas mixture was made up in the mixing bulb.

DMA	1.4 cm. Hg.
H_2	3.5 cm. Hg.
Total	4.9 cm. Hg.

This gave a reaction vessel pressure of 3.5 cm. Hg. total or 1 cm. Hg. of DMA.

A large number of runs was performed on gold wires between 320°C and 370°C, which seemed to be the limiting temperatures.

4.2c Results:

The results of the experiments fall into two very distinct groups,

i) Those performed below 355°C

ii) Those performed above 355°C.

A very clear dividing line occurs at this temperature.

i) Reactions below 355°C:

These reactions were all very similar having a ten minute "warm-up" period, followed by a period of relatively rapid reaction, which then rapidly decelerates, possibly due to self poisoning. This means that the reaction seldom passes the point at which 35% of the DMA has been hydrogenated/

hydrogenated. After twenty-four hours a reaction at 340°C had barely reached 40% reaction of DMA.

As the temperature was raised the "warm-up" period tended to decrease and the period of deceleration occurred earlier. The threshold of activity seemed to be in the region of 315 - 320°C but this was rather uneven. If the maximum reaction rate recorded was considered to be the true rate for the reaction then it is remarkable how little the rate varies with temperature. A series of nine performed between 330°C and 355°C revealed almost no variation in reaction rate, all being in the region of 0.5% min^{-1}. The rates as measured are listed below.

Reaction Temp. °C.	Reaction Rate % Min.
335	0.47
340 (i)	0.47
340 (ii)	0.43
345	0.39
347	0.46
350 (i)	0.55
350 (ii)	0.47
352	0.41
355	0.45

The products of the reaction are primarily the three linear butenes, but a trace of 1,3 butadiene was also obtained. The ratio of the butene products did not vary with temperature to any noticeable extent, and was fairly consistent from reaction to reaction, without showing any trends, nor/

nor did it vary during reaction. No isomerisation of the products occurred after hydrogenation had ceased. The mean ratios, from which no reaction varied to any significant extent were:

$$[\text{c-but-2-ene}] : [\text{t-but-2-ene}] : [\text{but-1-ene}] = 22 : 2 : 1$$

The 1,3 butadiene trace, rarely increased above 0.2% of the carbon analysed.

ii) Reaction above 355°C:

When the reaction temperature was raised above 355°C, although no other conditions were changed, a rather different reaction occurred. The beginning of the reaction was unchanged, in that there was an initial "warm-up" period of several minutes followed by an acceleration. This acceleration was not so great as that which occurred below 355°C. The linear portion of the curve was very short as the reaction rate began to drop off until it stopped at about 20 - 25% reaction of DMA.

This is not very startling, but the products are, being no longer merely butenes, but including a wide variety of isomerised and hydrocracked species, i.e. C_1, C_2, C_3 hydrocarbons and DMA isomers; in quantities comparable with those of the butenes. The following isomers of DMA have been detected, and identified by retention time

1,3 butadiene

methyl allene

The normal range of butenes has also been detected, as have the following hydrocracking products

methane

ethane

ethylene

propylene

methyl acetylene

There was another, as yet unidentified, product which occurred as a trace and which had a fairly long retention time on the column. It is difficult to see what this could have been although it may have been a polymer. The ethane probably occurs only as a trace which shows as distortion of the ethylene peak, causing the integrator to print sometimes. A typical analysis of one of these reactions is as follows:

Reaction at 358°C, gas composition after 70 minutes.

DMA	77%	
c-but-2-ene	13%	
t-but-2-ene	2%	
but-1-ene	0.7%	
1,3 butadiene	3%	
propylene	1%	
methane/ethane/ ethylene	4%	(overlapping peaks)
methyl acetylene	trace	
methyl allene	trace	
unknown peak	trace	

These percentages are expressed as the percentage of carbon atoms detected.

After seventy minutes the reaction was virtually stationary.

Because of the briefness of the fast period and the long retention time of some of the heavier more unsaturated gases it was impossible to estimate any reaction rates.

A wire which had been used for a reaction such as this would, after suitable reactivation, be active for the lower temperature reaction and could then be used for higher temperature reactions if this was desired.

If/

If the reaction temperature was raised above 375°C results similar to those in the region of 360°C were obtained. The reaction poisoned much more rapidly however, so that DMA reaction reached only 6 - 7% after two hours. After this the wire could not be satisfactorily reactivated. It would seem probable that further breakdown of the gases had occurred.

4.2b Reactions on another Sample of Gold Wire:

At the point reached above, the supply of gold wire came to an end, and a new supply was obtained from Johnson-Matthey, to the same specification.

This wire seemed to be less active than the previous sample, although its activity was of the same type. Below 355°C simple hydrogenation and isomerisation of the DMA to the usual butenes, 1,3 butadiene and trace of methyl allene occurred although reaction rates and final percentages of the reaction were rather less, only some 5 - 6% reaction occurring at maximum reaction rates in the region of 0.06% min^{-1}.

Above 355°C the production of butenes and isomers continued at a similar rate, while the production of traces of propylene and the methane/ethane/ethylene peak also appeared; maximum conversion of the DMA also fell in this case to 3 - 4%.

These reactions were carried out at a much later date than the preceeding ones.

4.3 The Hydrogenation of Dimethyl Acetylene on Expanded Gold Foil:

Some experiments were carried out on expanded gold foil which was activated between runs by the radio-frequency/hydrogen technique described for/

for palladium wires except that, obviously, the foil could not be degassed by electrical heating. Instead, it was considered probable that simply evacuating the foil at reaction temperature (in excess of 300°C) for thirty minutes would probably remove most of the hydrogen. Between runs, the foil was, of course, degassed overnight at 450°C.

The weight of the gauze was 0.0152 kg. and the geometric surface area probably lay between 0.04 - 0.05 m^2. The gas mixture made up in the mixing volume was the usual one

DMA	1.4 cm. Hg.
H_2	3.5 cm. Hg.
Total	4.9 cm. Hg.

The reaction vessel pressures were in the region of 3.5 cm. giving a pressure of DMA of 1 cm. Hg. at reaction temperature. The results of the experiments were very similar to those for gold wires, except that the catalyst was much less active. The reaction profile showed an initial burst of activity followed by rapid poisoning so that the system seldom got beyond 2% reaction of the DMA. The major product at all temperatures was always cis-but-2-ene, i.e. in the region of 320 - 370°C along with traces of the other butenes and 1,3 butadiene. At higher temperatures, i.e. above 350°C, traces of propylene also showed.

4.4. The Hydrogenation of Dimethyl Acetylene on Gold Films

4.4a The Preparation of Gold Films:

The method of preparation of the gold films was that described by Andersen (123) in which 0.25 m. of 2 x 10^{-4}m. diameter gold wire was wound evenly around 0.15 m. of 3 x 10^{-4}m. diameter tungsten wire. The gold wire was then cut at small intervals so that, in effect, a number of small lengths of/

of gold wire had been wound at intervals onto the tungsten wire. This assembly was then placed into position inside the reaction vessel and baked out overnight at 450°C. On the following morning a degassing current of 2.5A was passed through the wires for thirty minutes. The reaction vessel was then immersed in ice, and the current flowing through the wires was turned up until the gold wire fused and coalesced into beads of gold at intervals on the tungsten wire; this usually required a current in excess of 5A. The current was then turned down to 3.8A, at which point a gold film of about mass 2.10^{-5}kg. would be thrown in twenty minutes, although some wide divergencies from this film weight were obtained. The tungsten/ gold wire thus prepared could be used to throw up to three more films.

The activity of the film seemed to be independent of film weight but this is not surprising in view of Pritchard's (129) results for gold films thrown at 60°C which had a surface area of only twice geometric while films thrown at -183°C then raised to 60°C had surface areas only four times the geometric value.

It is worth commenting upon the appearance of the films thus produced which were, of course, a very pleasant soft yellow colour in their thicker regions but, as they thinned out near the edges this changed to the two complementary transmissions and reflection colours which are a deep rich purple and an equally powerful olive green. Low angle reflection showed up as light brick red colour. Altogether a phenomenon of great appeal and beauty.

4.4b/

4.4b Experiments on Gold Films:

The experimental runs, performed using gold films, fall into four neat groups.

i) Exploratory runs designed to discover suitable operating conditions for the films and the reproducibility of reactions on the films.

ii) Experiments to determine the apparent activation energy of the hydrogenation reaction.

iii) Experiments to determine the order of the reaction in hydrogen.

iv) Experiments to determine the order of the reaction in DMA.

i) Exploratory Runs:

A film was thrown as described, which weighed 58 mgms. (unusually heavy). The usual 2.5:1 mixture of hydrogen and DMA was made up in the mixing bulb and admitted at 0°C. The reaction vessel pressure was 3.2 cm/Hg. indicating a pressure of DMA equal to 0.92 cm. Hg. The temperature of the reaction vessel was steadily raised by means of an aeriated sand bath until reaction began in the region of 225°C; the reaction was very fast at 270°C. The reaction vessel was now pumped out and a new reaction mixture was admitted at 272°C; this reaction proceeded rather slowly. When a third reaction mixture was admitted to the outgassed film, also at 272°C, the reaction rate was negligible; after fifteen hours only some 8% of the DMA had reacted and there were traces of C_2 and C_3 gases (ethylene probably and propylene certainly). Both 1,3 butadiene and methyl allene were present.

A/

A new film, of mass 28.3 mgms., was prepared. This seemed to be very similar in properties to the first film. A run at 276°C was broadly similar to the initial experiment when it was run at 272°C, indicating that activity of the films was probably reproducible.

ii) The Apparent Activation Energy:

To obtain results suitable for an Arrhenius' Plot, a series of experiments was carried out in which a reaction mixture of gases, as described below, was admitted to a freshly thrown gold film at 0°C. The sand bath, already at the required reaction temperature, was then placed around the reaction vessel. The reaction rate was monitored in the usual fashion.

The reaction mixture as prepared in mixing bulb

DMA	1.4 cm. Hg.
H_2	3.5 cm. Hg.
Total	4.9 cm. Hg.

This gave a reaction vessel pressure of 3.2 cm. Hg. indicating that the DMA pressure was 0.92 cm. Hg. and the hydrogen pressure was 2.3 cm. Hg.

Experiments were carried out between 279°C and 322°C.

Results:

The reaction profile appeared to be that of slightly self-poisoning first order reaction. In view of other evidence, however, it is possible that in fact a strongly self-poisoning zero order reaction occurs. The products are primarily the linear butenes, with cis-but-2-ene predominating, traces of butane, 1,3 butadiene and methyl allene also occur.

DMA/

DMA Reaction

Temp. °C	Temp. °A	$\frac{1}{T} \times 10^3$ $^{\circ}A^{-1}$	Film Wgt. mgms.	Rate % min^{-1} initial	Log_{10} Rate
279	552	1.812	15.5	0.708	$\bar{1}.8500$
288	561	1.783	57.2	0.821	$\bar{1}.9143$
298	571	1.751	53.9	0.968	$\bar{1}.9859$
303	576	1.736	16.3	1.154	0.0607
322	595	1.681	49.4	1.356	0.1335

Arrhenius gradient = $\frac{0.40}{0.183 \times 10^{-3}} = 2.18 \pm 0.15 \times 10^3$

∴ From the Arrhenius' equation, the apparent activation E_A is given by

$$E_A = \frac{0.40}{0.183} \times 1.987 \times 2.303 \text{ k.cals. mole}^{-1}$$

$$= 10.0 \pm 0.6 \text{ k.cal. mole}^{-1}$$

$$\therefore E_A = 42.0 \pm 2.5 \text{ k.j. mole}^{-1}$$

$\frac{1}{T} \times 10^3$ $^{\circ}A^{-1}$	cis-but-2-ene Rate % min^{-1}	cis-but-2-ene Log_{10} Rate	trans-but-2-ene Rate % min^{-1}	trans-but-2-ene Log_{10} Rate	but-1-ene Rate % min^{-1}	but-1-ene Log_{10} Rate
1.812	0.506	$\bar{1}.7842$	0.111	$\bar{1}.0453$	0.047	$\bar{2}.6721$
1.783	0.633	$\bar{1}.8014$	0.164	$\bar{1}.2148$	0.032	$\bar{2}.5051$
1.751	0.732	$\bar{1}.8645$	0.185	$\bar{1}.2672$	0.059	$\bar{2}.7709$
1.736	0.819	$\bar{1}.9133$	0.244	$\bar{1}.3874$	0.067	$\bar{2}.8261$
1.681	1.000	0.000	0.294	$\bar{1}.4683$	0.082	$\bar{2}.9138$

cis-but-2-ene

Arrhenius gradient $= -2.12 \pm -.08 \times 10^3$

$\therefore$ as above

$E_A = 2.12 \times 1.987 \times 1.202$ k.cal.mole^{-1}

$= 9.7 \pm 0.4$ k.cal. mole^{-1}

$= 40.7 \pm$ k.j. mole^{-1}

trans-but-2-ene

Arrhenius gradient $= 2.18 \pm 0.3$

$\therefore E_A = 2.18 \times 1.987 \times 1.303$

$= 10.0 \pm 1.3$ k.cal. mole^{-1}

$= 42.0 \pm 5.4$ k.j. mole^{-1}

but-1-ene

Arrhenius gradient $= 2.64 \pm 0.2$

$\therefore E_A = 2.64 \times 1.987 \times 2.303$

$= 12.1 \pm 0.9$ k.cal. mole^{-1}

$= 50.8 \pm 3.8$ k.j. mole^{-1}

The calculated apparent activation energies may then by tabulated

Plot	E_A K.cal.mole^{-1}	E_A k.j.mole^{-1}
DMA reaction	10.0 ± 0.6	42.0 ± 2.5
c-but-2-ene production	9.7 ± 0.4	40.7 ± 1.7
t-but-2-ene production	10.9 ± 1.3	42.0 ± 5.4
but-1-ene production	12.1 ± 0.9	50.8 ± 3.8

Product/

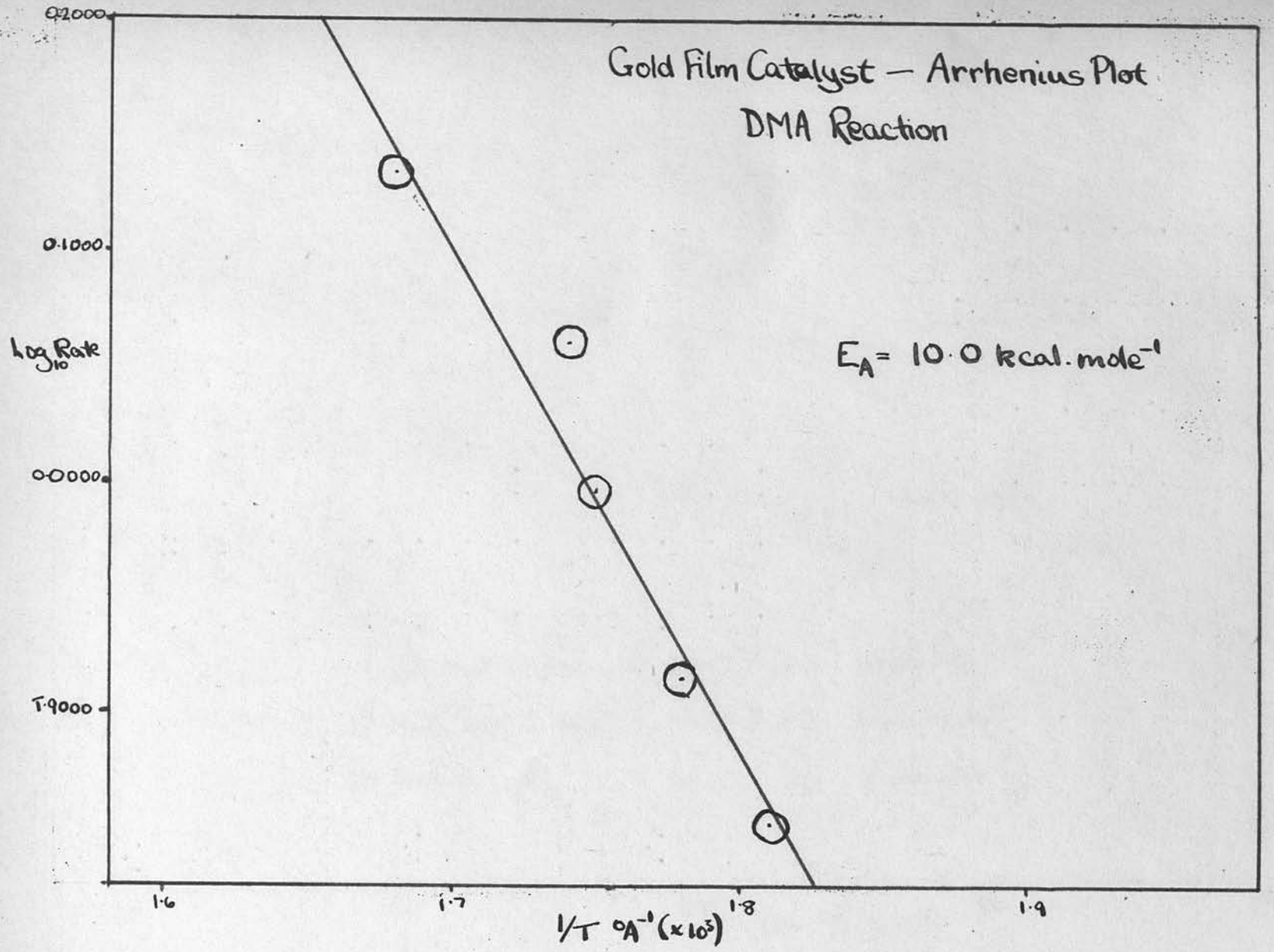

Gold Film Catalyst — Arrhenius Plot
DMA Reaction
E_A = 10·0 kcal.mole^{-1}
0·2000
0·1000
0·0000
T·9000
Log$_{10}$ Rate
1·6
1·7
1·8
1·9
1/T °A^{-1} (x10^3)

Fig 10

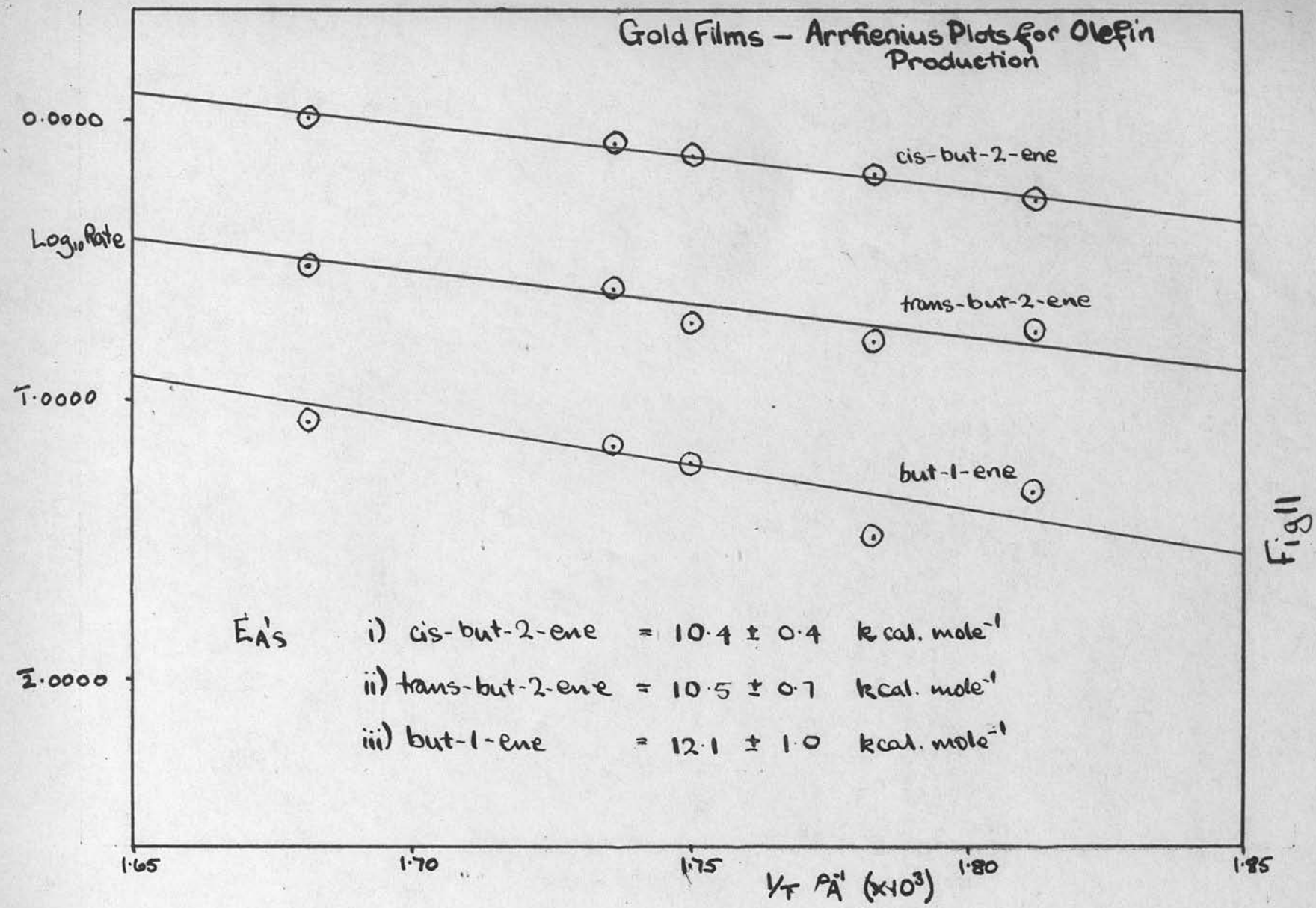

Gold Films – Arrhenius Plots for Olefin Production
cis-but-2-ene
trans-but-2-ene
but-1-ene
0·0000
Log10 Rate
T·0000
Σ·0000
1·65
1·70
1·75
1·80
1·85
1/T °A⁻¹ (x10³)
EA's
i) cis-but-2-ene = 10·4 ± 0·4 k cal. mole⁻¹
ii) trans-but-2-ene = 10·5 ± 0·7 kcal. mole⁻¹
iii) but-1-ene = 12·1 ± 1·0 kcal. mole⁻¹

Fig II

Product Selectivity

The selectivity of the reaction is summed up in the table below in terms of the cis-trans ratio and the selectivity coefficient s, where

$$s = \frac{\text{conc. cis-but-2-ene}}{\text{total conc. of butenes and butane}}$$

Temp. ^{o}C	cis/trans	S
279	4.0	7.79
288	3.9	7.68
298	3.9	7.49
303	3.9	7.49
322	3.4	7.37

This indicates a general fall off of selectivity with temperature increase; the anomalous "s" value for the reaction at 303^{o}C is due to an unusually high production of but-1-ene.

iii) The Order of Reaction in Hydrogen:

To determine the order of the reaction in hydrogen, a series of experiements was performed at 291^{o}C in which the partial pressure of DMA was kept constant while that of hydrogen was varied so that the ratio of the pressures of hydrogen and DMA changes from 0.79:1 up to 7.71:1; i.e. the hydrogen pressure was varied by a factor of almost ten.

The initial rate of each reaction was determined along with the ratio of the cis- and trans-but-2-ene and s, where s is a selectivity factor defined as in part (ii).

The/

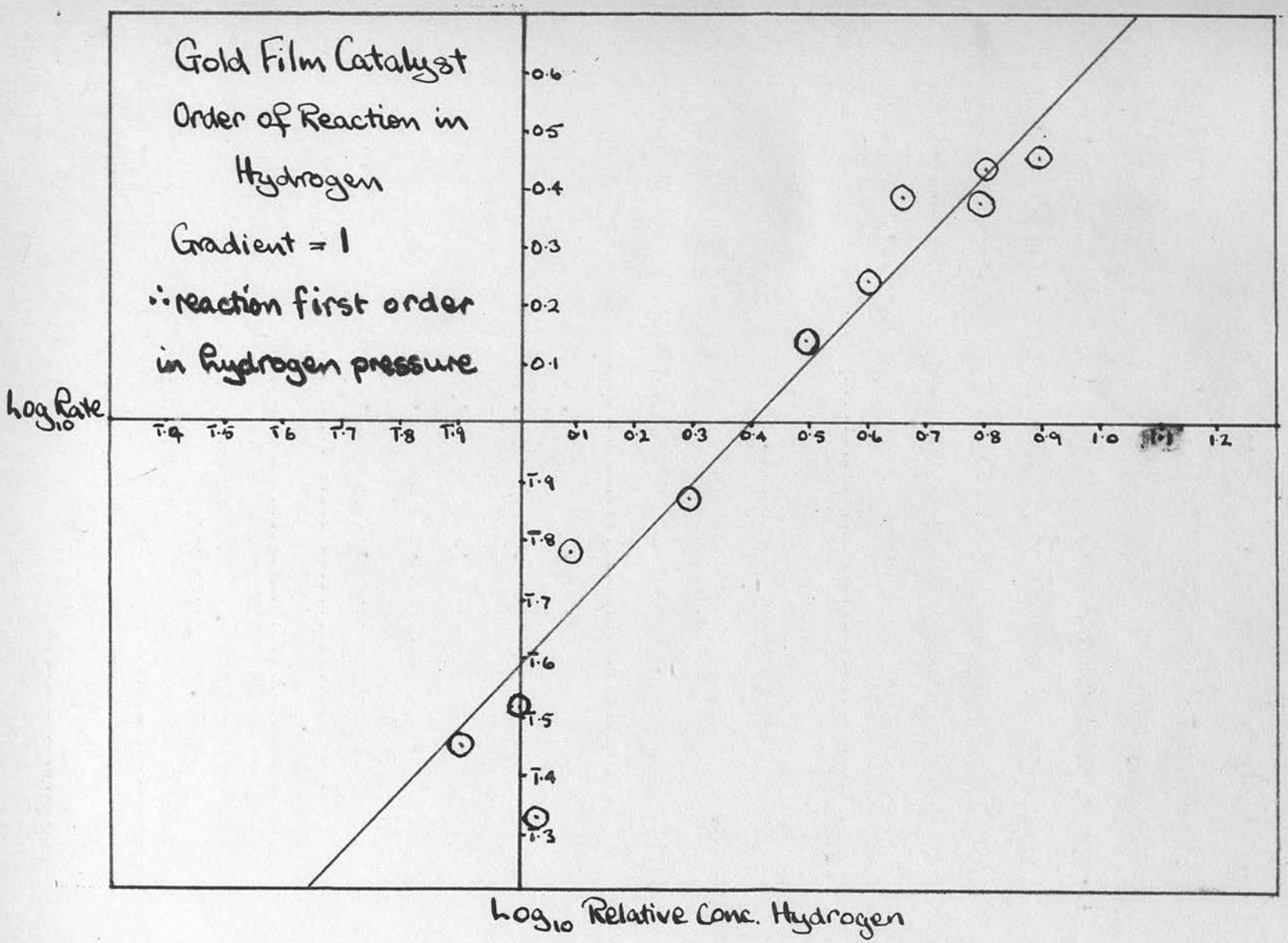

Gold Film Catalyst
Order of Reaction in Hydrogen
Gradient = 1
∴ reaction first order in hydrogen pressure
Log10 Rate
Log10 Relative Conc. Hydrogen
0·6
0·5
0·4
0·3
0·2
0·1
T·9
T·8
T·7
T·6
T·5
T·4
T·3
T·4
T·5
T·6
T·7
T·8
T·9
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2

Fig 12

The DMA pressure in the mixing bulb was always 1.4 cm. Hg. and the hydrogen pressure was as appropriate for the required ratio. The gases were admitted at reaction temperature which gave a reaction vessel pressure of DMA equal to 1.1 cm. Hg.

Film weight mgms.	DMA : H_2	Initial Rate $\%min^{-1}$	cis-trans	S
21.8	1 : 0.79	0.28	0.82	0.453
16.6	1 : 1.00	0.32	0.75	0.455
14.6	1.: 1.07	0.21	2.54	0.662
21.9	1 : 1.22	0.60	1.34	0.538
48.2	1 : 1.93	0.74	1.50	0.573
34.7	1 : 3.07	1.38	5.4	0.832
31.0	1 : 3.93	1.75	2.66	0.669
38.6	1 : 4.60	2.45	5.90	0.843
28.0	1 : 6.07	2.35	2.92	0.723
24.9	1 : 6.21	2.70	3.50	0.715
15.6	1 : 7.71	2.83	4.50	0.792

These results show clearly that the reaction is first order in hydrogen over gold and that the selectivity shows a general increase as hydrogen partial pressure increases.

iv) <u>The order of Reaction in DMA</u>:

A series of reactions was performed at 288°C in which the hydrogen partial pressure was kept at a constant value, while the partial pressure of/

of DMA was varied. The partial pressure of hydrogen in the mixing bulb was always 3.5 cm. Hg. which gave a reaction volume pressure of 2.8 cm. Hg. In other respects the reaction was performed as in part (iii).

Film weight mgms.	DMA : H_2	Initial rate $\%min^{-1}$	Corrected molar rate	cis/trans	S
27.2	0.5 : 2.5	2.00	1.00	2.5	0.65
57.2	1 : 2.5	0.82	0.82	3.8	0.75
27.2	2 : 2.5	0.51	1.02	3.9	0.82
24.7	3 : 2.5	0.23	0.69	2.5	0.68
26.8	3.6 : 2.5	0.18	0.66	1.9	0.62

The corrected molar rate is defined as the initial rate corrected for molar conc. of DMA, i.e. it is obtained by multiplying the initial rate by a factor equal to the DMA : H_2 ratio expressed in this case by $[H_2] = 2.5$

The order of reaction in DMA was determined by plotting log molar rate vs. log conc. DMA

since $\text{Rate} = k[DMA]^x$

$\therefore \log \text{rate} = x \log [DMA] + c$

$\therefore$ the gradient of the plot = x

$\therefore$ the reaction order is x

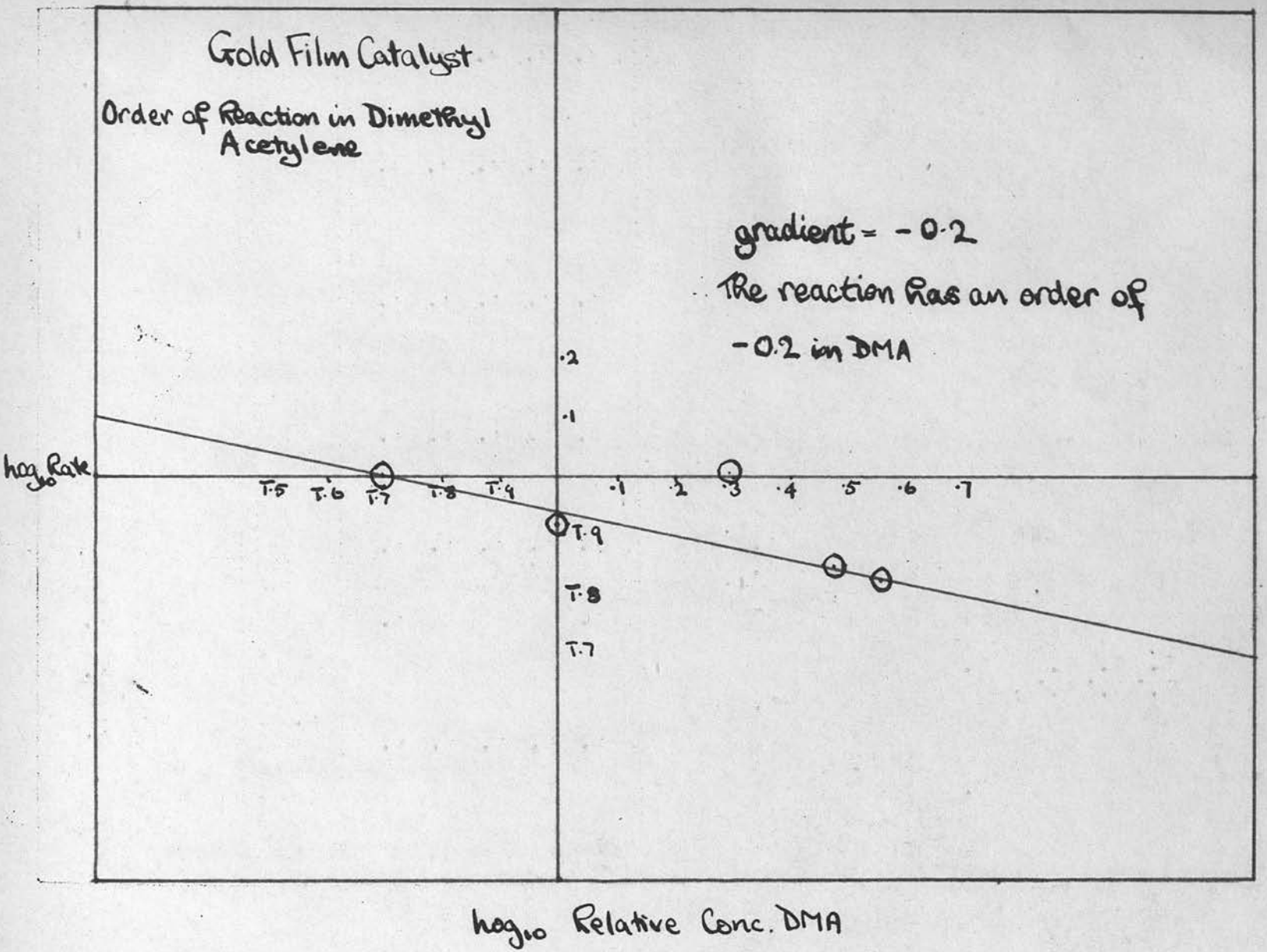

Gold Film Catalyst
Order of Reaction in Dimethyl Acetylene
gradient = -0·2
The reaction has an order of -0.2 in DMA
log10 Rate
·2
·1
T·5
T·6
T·7
T·8
T·9
T·9
T·8
T·7
·1
·2
·3
·4
·5
·6
·7
log10 Relative Conc. DMA

Fig 13

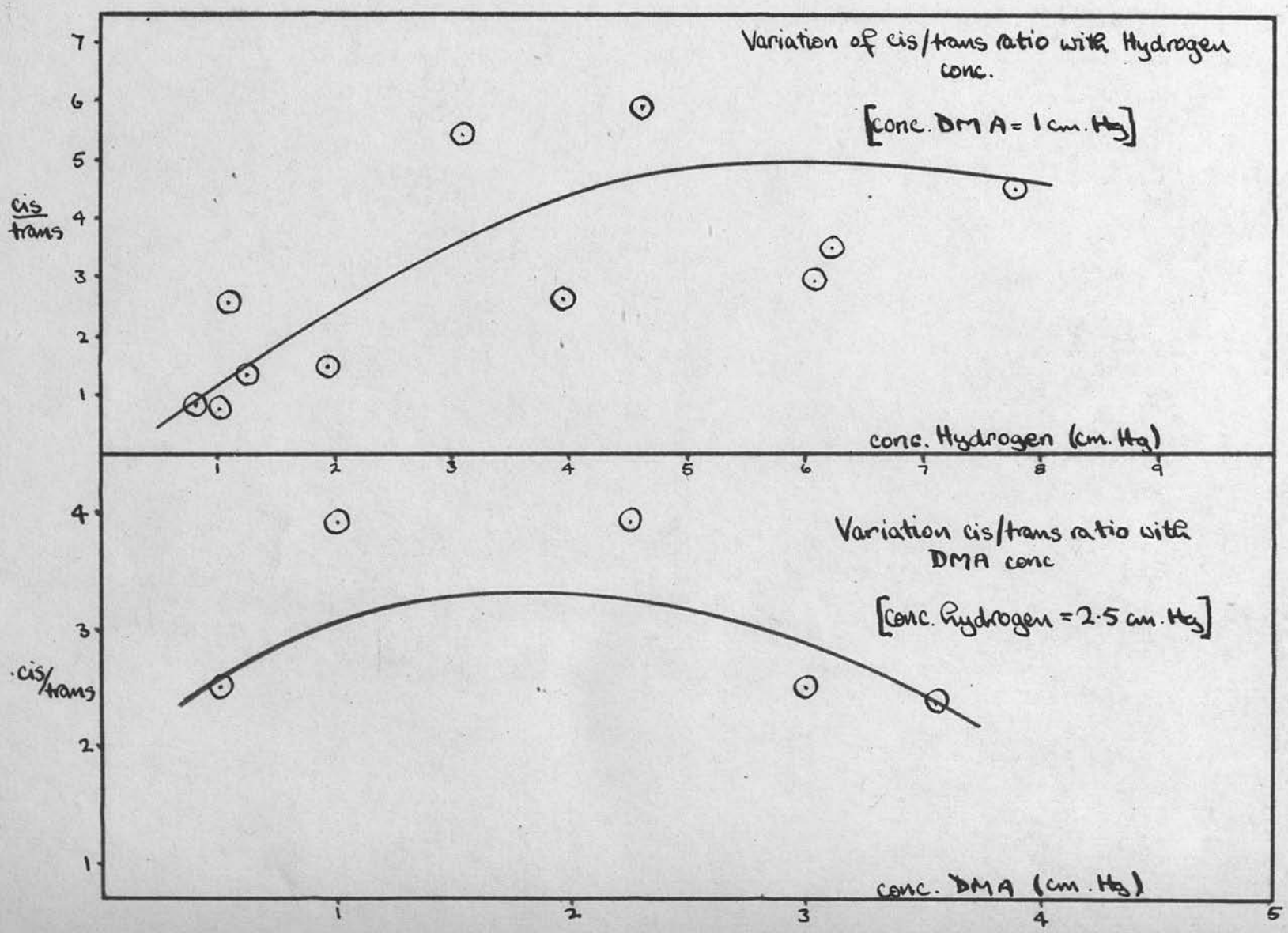


Fig 14

Gold Films

Relative [DMA]	Log_{10} rel.[DMA]	Molar rate	Log_{10} molar rate
0.5	1.6990	1.00	0.0000
1	0.0000	0.82	1.9138
2	0.3010	1.02	0.0086
3	0.4771	0.69	1.8388
3.6	0.5563	0.66	1.8195

The gradient of this plot is -0.2. Therefore the reaction order is -0.2 in DMA.

v) Control Experiments

a) A run was carried out at 340°C on a fresh film in which only 1 cm.Hg. pressure of DMA was admitted. No significant reaction occurred. After 24 hours small traces of butenes were noticed, indicating that self hydrogenation was not significant. There was no isomerisation.

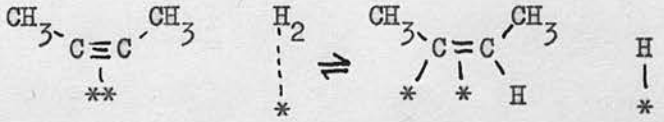
b) A run on a fresh film at 370°C, in which a 2.5 : 1 hydrogen : DMA mixture was used (reaction vessel pressure of DMA approximately 1 cm. Hg.) gave very rapid hydrogenation of DMA to butenes and butane until some 12% of the DMA had reacted, at which point the reaction literally stopped. Traces of propylene and DMA isomers also occurred.

c)/

c) A run was performed at 335°C using only a tungsten wire which had been treated exactly as the more usual tungsten/gold wire. The rate of hydrogenation of the DMA was minimal, i.e. 0.01 % min^{-1}.

4.5 Discussion:

The facts which emerge from this work certainly emphasize the unusual nature of the gold catalyst. To begin with, the most unexpected property encountered is its ability to hydrocrack DMA. This is almost certainly a complex reaction and one for which much more information would be needed before any definite conclusions could be drawn and it may well be connected with the associated isomerisation reactions; i.e. hydrogenolysis may occur at intermediate stages of the isomerisation. It was shown, however, that isomerisation does not occur in the absence of hydrogen on gold films, nor was any trace of propylene noticed. Almost certainly then reaction begins with the addition of a hydrogen atom to adsorbed DMA, leading to an adsorbed substitute vinylic intermediate. /The hydrogen atom will almost certainly come from a physically adsorbed hydrogen molecule/ This may be followed by hydrogen abstraction, or by further hydrogen action to give but-2-enes.

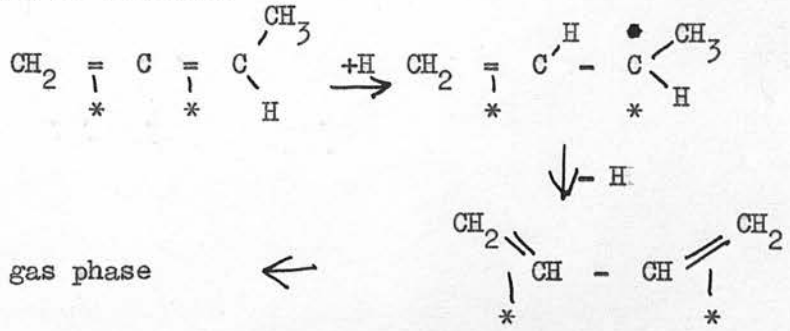


(or similar species)

gas phase

which is adsorbed methyl allene

The adsorbed methyl allene can easily act as a source of 1,3 butadiene, as follows:



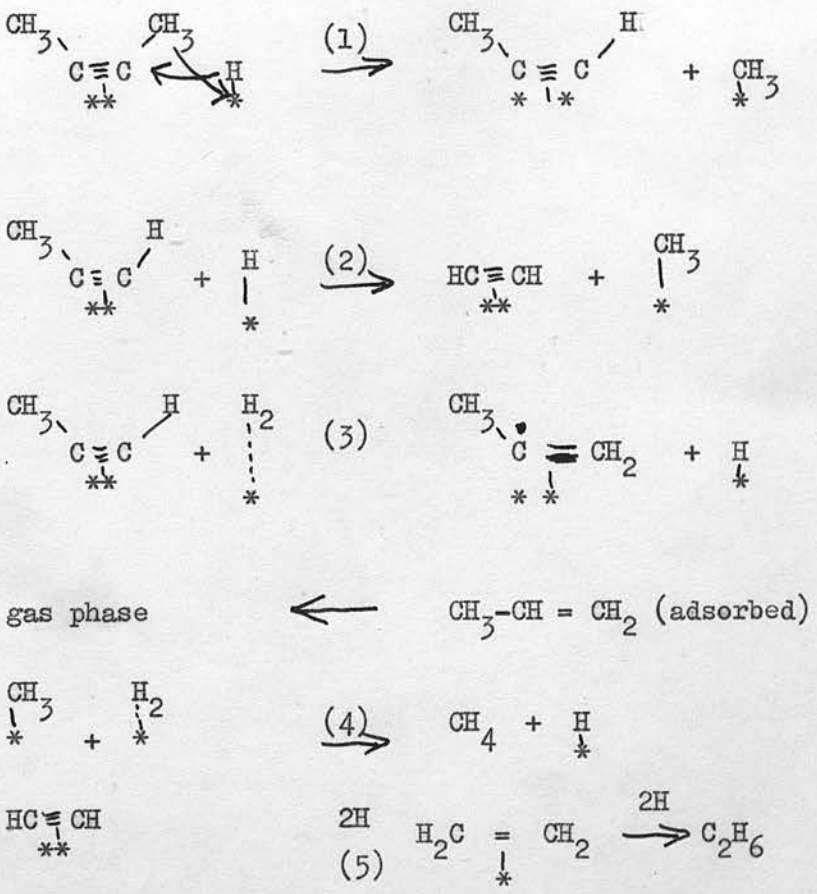
i.e. adsorbed 1,3 butadiene

Both these products are observed not only here but also for many of the alloy wires (see next chapter).

When considering the hydrocracking reaction the whole range of products should be considered since these are probably all formed via similar reaction routes.

The products observed are CH_4, C_2H_6, C_2H_4, C_3H_6 and C_3H_4, hence the mechanism proposed should account for all these products. The obvious route is via a simple fission of the bond between a methyl group and an acetylenic carbon, possibly under the influence of an adjacent hydrogen species. This would readily account for the trace of methyl acetylene and for the formation of methane. Subsequent hydrogenation of adsorbed methyl acetylene could lead to the formation of propylene while alternatively, fission of the other methyl group - acetylenic bond could lead to the formation of more methane and also adsorbed C_2 species. The state of any hydrogen involved in the fission reaction is of interest; it may be that a physically adsorbed molecule of hydrogen forms some sort of activated complex, or possibly some hydrogen atoms on the surface may be involved/

involved. In view of the proposed mechanism for isomerisation, which fits in well with the known properties of gold as a hydrogenation/dehydrogenation catalyst, there may be an unusually high concentration of surface hydrogen atoms. Another factor is temperature. The postulated d-s promotion mentioned in 4.1 is temperature dependent, so that as temperature rises, the concentration of d-band vacancies will also rise, thus increasing the ability of the gold to stabilise any surface hydrogen species. In view of this, it is suggested that a surface hydrogen atom is involved.



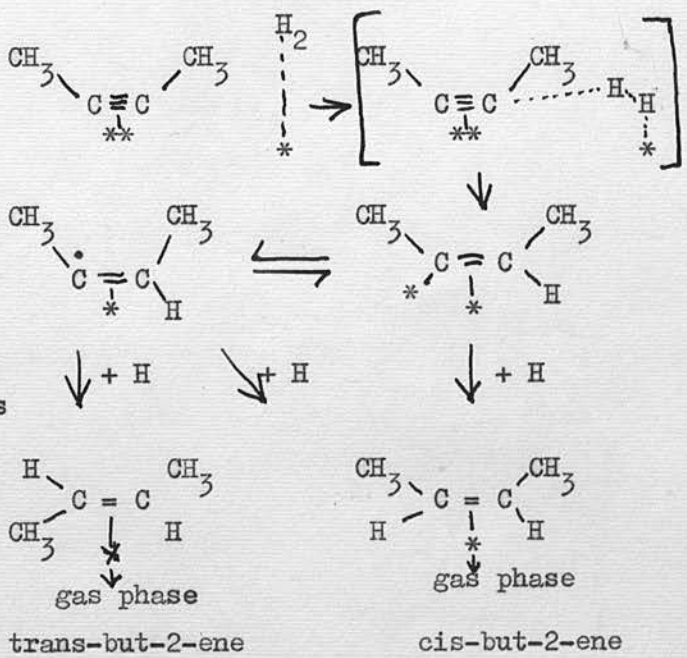
All the known products are thus produced.

The/

The simple hydrogenation of DMA to butenes will almost certainly be the same on both wires and films and will almost equally certainly involve a stepwise addition of hydrogen atoms to the adsorbed molecule.

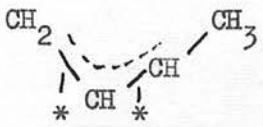
On gold films the reaction has orders of one in hydrogen and -0.2 in DMA. The reaction profiles show that the reaction appears to be self poisoned zero order when the relative concentration of hydrogen is high and rather intermediate highly self-poisoned zero or first order, when the hydrogen concentration is lower. The high degree of poisoning is more probably because of side reactions than annealing of the film since it seems unlikely that a sufficient degree of annealing could be accounted for in terms of surface area changes. It seems to be much more likely, on balance, that either polymerisation of the 1,3 butadiene produced by isomerisation, or strongly adsorbed highly dehydrogenated surface species, or possibly both, are responsible. In view of the small number of active sites, which gold can possess, it should be very easy to poison.

For the production of linear butenes on gold the following mechanism is proposed:



Production of but-1-ene could well occur via the hydrogenation of adsorbed dienes which could occur as previously described. The hydrogenation of adsorbed species such as these would give a mixture of linear butenes, possibly via π-bonded allylic species.

e.g.



The cis-trans ratio and the selectivity coefficient s are of interest in this context. These figures obtained from experiements to determine the reaction order both show a maximum for selectivity in the middle region of the hydrogen/DMA ratios studied, indicating that selectivity tends to fall off when the concentration of hydrogen is either high or low with respect to that of DMA. It is not surprising that a high concentration of hydrogen should produce a low selectivity since this will increase the surface coverage of hydrogen, thus aiding butane production and hydrogen transfer reactions. The low selectivity at low hydrogen concentrations is probably best explained in terms of the life time of certain surface species. As the coverage of hydrogen decreases then the lifetime on the surface of half hydrogenated species will increase, thus improving the change of isomerisation reactions at the expense of further immediate hydrogenation. This would be true of any of the mechanisms described above. Isomerisation will increase the probability of trans-but-2-ene and but-1-ene formation at the expense of cis-but-2-ene. Indeed it will be noted, that for some of the ratios of hydrogen/DMA used in hydrogen reaction order investigations, trans-but-2-ene is the major product. The reaction orders of one for hydrogen and -0.2 for DMA also fit/

fit in well with this picture, as the very strongly adsorbed DMA allows only a very small coverage of hydrogen at the surface, probably only in spaces left by the surface packing of the DMA.

The reaction rates measured for gold wire experiments, as was mentioned, varied very little. This is perhaps not too surprising. At the temperatures involved and, considering the small number of active sites available, it seems quite possible that the reaction is diffusion controlled; i.e. the rate limiting step will be connected with the rates of molecules arriving at, or leaving, the surface. In this connection Holden and Rossington's report of ortho para-hydrogen conversion, in which rate was unaffected by pressure, over gold (133) is of interest. This no doubt is a related phenomenon.

Gold then has once more proved itself to be catalytically unusual. It comes as no real surprise that, under extreme conditions, it can hydrogenate DMA and as was even more likely, isomerise DMA in the presence of hydrogen. In view of the small number of active sites which gold must possess, the fact that it can strongly and irreversibly poison itself is also unsurprising. Its hydrocracking properties are really surprising, though, and it is difficult to explain this in terms of any known property of gold. Much more remains to be discovered with regard to this phenomenon.

CHAPTER 5.

THE HYDROGENATION OF DIMETHYL ACETYLENE ON PALLADIUM-GOLD ALLOY WIRES

5.1 The Activation of Alloy Wire Catalysts:

The initial aim of this research project was the study of the variation of the catalytic activity of alloy wires with composiion, for the hydrogenation of DMA. In the first instance, this was to be done by observing the changes in apparent activation energy, and in frequency factor, over the alloy series. To achieve this, it was essential to obtain reproducible results, in terms of reaction rates, for experiements carried out under identical conditions. It is probably true to say that the greater part of the three years spent on this research project has been ~~to~~ devoted to this end, the development of a technique which produced useable results.

When this work began, it seemed theoretically attractive and practical to take an alloy wire, mount it in the reaction vessel and then heat it to dull red incandescenee in, say, 1 cm. Hg. pressure of oxygen. A treatment such as this should remove most of the likely surface contaminants such as grease, dust, carbon etc. as combustion products. If the oxygen were removed after some suitable experimentally determined time and replaced by hydrogen, then the no doubt partially oxidised surface would be reduced; i.e. strongly adsorbed oxygen would be removed as water and possibly any remaining contaminants would be removed as methane or hydrogen sulphide. After suitable degassing then, theoretically, there is no reason why the new cleaned surface should not be active in a reproducible fashion. As Duell and Robertson (138) have noted, however, simply/

simply "flashing" wires, as this technique is known, does not necessarily produce a thermodynamically stable crystal structure in the wire, so that quite small variations in cooling time or temperature gradients can cause marked differences in initial activity of the wire.

The first experiements were carried out, using an 0.01 m. length of 83% palladium 17% gold wire which was fitted into position in the reaction vessel and then degassed overnight at 450°C. It was then flashed for five minutes, first in oxygen and then in hydrogen of 1 cm. Hg. pressure, at dull red incandescence. After this the wire was degassed for twenty minutes, also at dull red incandescence. This made the wire catalytically active for the reaction (1 cm.Hg. DMA, 2.5 cm.Hg. hydrogen) in the region of 200°C.

It appeared to be impossible to reactivate the wire to the same degree however. Usually the wire appeared to deactivate with time although the reverse sometimes appeared to occur. Experiments conducted with 0.15 m. lengths of 100% palladium wire gave a generally similar picture.

A large number of experiments was performed, on the alloy wire, in which the length and severity of the activation processes were varied. No coherent picture seemed to emerge. Consecutive runs on a wire; without intermediate activation other than pumping down overnight, were performed. This gave some remarkably confusing results in that some reactions began to accelerate after an hour or so of slow reaction while others did not.

An attempt was made to activate wires by degassing overnight at 450°C, admitting 1 cm.Hg. pressure of hydrogen and leaving for two hours, after which/

which the reaction vessel was pumped down for thirty minutes. The system was then cooled to the reaction temperature and the reaction carried out: this gave relatively slow reactions at variable rates. From all these runs, and a number of others which were performed under similar conditions, no clear pattern emerged. It would appear that the factors which affect the activity of the surface are complex and possibly counteracting. When these experiments were being performed it seemed likely that factors which affected the activity were possibly:

i) Hydrogen poisoning, although it was not realised just how stubborn some of the adsorbed hydrogen could be.

ii) Slight variations in the pretreatment of the wire; leading, perhaps, to differences in the fraction of the surface area which was activated; i.e. end pieces of the wire may not be activated.

iii) Crystal faults in the wire which may be annealed by either chemical or thermal means (138); it seemed quite possible that thisfactor could vary from run to run.

iv) The previous chemical history of the surface. Generally a catalyst tended to become less active with use.

v) Residual pressure after the wire had been baked out did seem to vary, from near "sticking" vacuum, to 2×10^{-6} τ. The geometrical area of 0.1 m. of 2.8×10^{-4} m. diameter wire is approximately 9×10^{-5} m^2. A pressure of oxygen in the region of 10^{-6} τ could just about form a monolayer. This means that since/

since the surface area is tiny, apparently insignificant pressure changes may be of importance to the activity of the surface.

In retrospect, the above factors are probably all of importance, although, obviously, (i) and iv) are connected, but polymerisation reactions may also be important to (iv). In the activation technique eventually employed these were effectively eliminated. As will be seen, however, the results obtained were still far from perfect and it would seem likely that (ii) and particularly (v) were still of importance.

A sixth factor, which emerged later, and was probably the cause of much of the confusion encountered in the above work, was the high vapour pressure of palladium, at relatively low temperatures. It was discovered that a palladium wire at dull red heat can, in thirty minutes, deposit enough atoms on the reaction vessel walls for them to be significantly active catalytically and yet be invisible to the unpractised eye. This will be discussed later.

As a result, it was decided to attempt to activate the wires using an adaption of the method described by Couper and Eley (85), using the R.F. generator described in Chapter 2 to produce a discharge in low pressure hydrogen around the wire.

For these experiments 0.15 m. lengths of palladium wire were employed. Such wires, on activation by the flashing technique, had been active at 300°C, giving a quickly self-poisoning reaction yielding mainly cis-but-2-ene, with fairly large quantitites of the other linear butenes, 1,3 butadiene, methyl allene and another small unidentified peak.

The/

The wire was activated as follows. After the wire was fixed in position 1 mm. Hg. pressure of hydrogen was admitted to the reaction vessel, the R.F. output coil was placed around the reaction vessel, and the whole was immersed in liquid nitrogen. After allowing several minutes for equilibration, the generator was tuned, the discharge begun and allowed to continue for five minutes. The liquid nitrogen bath and the coil were then removed and the wire was pumped down for twenty minutes at room temperature at which time it was considered to have been activated.

A standard run (H_2 : DMA = 2.5 : 1) was carried out at 319°C on this wire; all DMA was hydrogenated within five minutes.

The reaction vessel was then evacuated for 30 minutes, at 319°C and a fresh reaction mixture was admitted. On this occasion the reaction proceeded much less quickly, some sixty minutes being required for complete hydrogenation of the DMA. After fifteen minutes, or so, some 5% of the DMA had been isomerised to 1,3 butadiene, traces of methyl allene also appeared. Little or no butane was produced.

The wire was then degassed overnight at 450°C and reactivated. A run at 284°C showed an activity similar to that of the first experiment.

After further degassing and reactivation, the wire was used for three runs at 247°C without intermediate treatment other than pumping down for 30 minutes at reaction temperature. In each case the DMA disappeared in around seven minutes. The subsequent isomerisation of the butenes to their thermodynamic ratios, and their hydrogenation to butane, did show a marked decrease from run to run, hydrogenation being rather more/

more poisoned than isomeriation. It seems likely that the reaction of the DMA is diffusion controlled at this temperature.

As a result of this, the wire was degassed at 450°C overnight and a run done at 119°C. This gave complete reaction of DMA in about sixteen minutes.

A subsequent run at 98°C after 30 minutes of pumping down, gave a reaction of 50% of the DMA in seventy-five minutes. In both these runs cis-but-2-ene was the major product, the only other products being trans-but-2-ene, and but-1-ene in trace amounts.

The wire was now showing signs of irreversible poisoning and a series of runs in the 80 - 90°C region showed progressive loss of activity.

It seemed likely that hydrogen poisoning was of some importance, and so some runs were done on a new wire which was reactivated between runs, after overnight degassing at 450°C. Instead of simply pumping down the wire, for twenty minutes, the wire was heated to dull red incandescence while the pumping was carried out. This increased the activity of the wire, so that it was active in the region of 0°C. It still showed a progressive loss of activity however.

It was decided, therefore, to try a series of runs in which a new 0.15 m. length of wire was used on each occasion, degassed and activated as described. This series of runs, in the region of 0°C, showed promise, in that some 50% of them appeared to follow, to within a factor of two or three, a change of reaction rate with temperature which would fit in with the/

the Arrhenius equation. Sometimes though, the wire appeared to be superactive, the reaction rate some twenty times greater than might have been expected. Eventually it was noticed that a wire which had deformed during baking out so that the loop was almost touching the reaction vessel walls, had deposited a visible trace of palladium on the vessel wall, at the point nearest to contact. Investigation showed that on turning up the degassing current "hot spots" appeared in the wire, it seems likely that these caused deposition of metal.

To overcome this difficulty, the obvious solution was to degas the wire at a lower temperature for a longer time. Current in the region of 1.8A had been needed to produce a full redness in the wire, so it was decided to use a current of 0.9A for a period of ninety minutes.

The percentage of experiments in the "reproducible" class increased markedly, but some superactivity still occurred. At this time, some difficulty was being encountered in the operation of the R.F. generator, which tended to behave in a tempramental fashion. This was eventually traced to a faulty A.C. choke, and when this was replaced the number of superactive wires rose again.

It was possible that when the R.F. generator was operating at full power, it could heat the wire enough to cause deposition. To test this hypothesis a wire was inserted and the generator was left running for 45 minutes, at the end of this time a faint film of palladium was plainly visible.

Obviously, the output of the generator, which had almost certainly been varying because of the fault, had to be measured and thedevice shown in/

in Chapter 2 was obtained. This indicated a current of 3.5 mA. when it was fixed in place with its aerial some 18 inches from the output coil of the generator operating at full power.

A series of runs was performed with the output power of the generator varied systematically, the discharge being run for ten minutes in each case. These runs clearly demonstrated the onset of palladium deposition. All these runs were done using the Pd:Au = 83:17 alloy, at 30°C.

Milliammeter reading	Max. rate Å min $^{-1}$
1	0.13
2	0.11
2.5	0.34
3.5	0.78

This indicates rather clearly that deposition begins above 2mA. Later experience showed that even an output power sufficient to give a reading of less than 2mA could produce palladium films, probably because of hot spots on the wire. It was found that if the power was kept between the limits which produced readings of 1mA and 1.5mA., superactivity occurred infrequently.

It is interesting to note that these very fine palladium films were virtually invisible in direct daylight or artificial lighting. Diffuse light, such as that which was found at the foot of the white painted stair wells in the chemistry department, often showed the pale grey shadows quite clearly.

There/

There still remained a fairly large number of relatively inactive catalysts, which were more difficult to deal with. One variable not previously mentioned, is the pressure of hydrogen used for the discharge. Obviously there was a preferred value for this and variations might explain some of the less active catalysts. A subjective method was adopted for reaching the ideal value. An excess of hydrogen was allowed into the reaction vessel and left for three minutes at liquid nitrogen temperature. The R.F. generator was then tuned to full power and hydrogen was slowly removed from the reaction vessel until discharge just began. The output power of the generator was then reduced to the chosen value and more hydrogen was removed from thereaction vessel. The ideal pressure was chosen as that at which an intense halo of purple light surrounded about two thirds of the length of the wire. If more hydrogen was removed then the discharge became a gentle pink glow general to the whole reaction volume, which did not activate the wire so well. For activation, the discharge was continued for ten minutes. This method seemed to be preferable to using prechosen pressures which, in view of their small magnitude were difficult to obtain and, in any case, did not always produce the same type of dishcarge. The position of the output coil was very critical to the discharge, as possibly was the position of the wire, which tended to warp during the baking out process.

Even after all this, some 30% of the runs were useless, mostly because of low activity. This may be attributed to several factors.

i) variable residual pressures after bake-out.

ii) variable quantities of impurities in the reaction gases which might/

might not have been important had higher active surface areas been involved.

iii) perhaps the past history of the catalysts had led to differences in the potential surface activity of the catalyst, e.g. exposure to oil or mercury.

Of these, the second is a very likely explanation and one which can be used to explain some of the experimental results. At the levels of impurity involved, it was difficult to do anything about further purification.

In conclusion it must be said that the alloy wire catalysts used are, with respect to the reaction, unusually delicate. This of course, stems from the low surface area of the wires, and possibly also the surface is not chemically fresh, i.e. a different wire is used for each experiment and, since the surface is not completely new, any differences in the history of the surface could be critical. Traces of oil, dust or finger grease may not be entirely removed and remain as poisons, or a trace of mercury may act as a poison or an annealing agent.

The question of annealing is also important since changes in surface area over the range of alloys will obviously affect the apparent frequency factor. Gold, at the temperatures involved will probably anneal its surface to near thegeometric value (128, 129) while palladium, being much harder, less ductile metal, will not (95), and it is probable that the true surface area will be several times that of gold. Just how this varied over the alloy series is difficult to say, but the effect would undoubtedly be reduced by the degassing procedure, which will anneal the wires considerably:

The/

The procedure for each wire is as follows -

i) Overnight degassing/baking out at 450°C.

ii) Activation (R.F. generator/Hydrogen, 10 minutes).

iii) Degassing (90 minutes at 0.9 A).

5.2 The Hydrogenation of Dimethyl Acetylene on Alloy Wires

The Experiments:

All runs designed for Arrhenius Plots were done using a standard gas mixture, made up in the mixing bulb as follows:

DMA	1.4 cm. Hg.
H_2	3.5 cm. Hg.
Total	4.9 cm. Hg.

i.e. H_2: DMA = 2.5:1

The reaction mixture was admitted quickly at reaction temperature. The errors arising from this were very small, the reaction vessel pressure varying by less than $\pm$ 0.1 cm. Hg. for each alloy. The total change in reaction vessel pressure over the whole range of temperatures (0 - 300°C) as 0.5 cm. Hg.

In fact, since the time for admittance of thereactants was very short, the variation of the number of moles in the reaction vessel was small. Certainly the sample size tended to grow quite rapidly, as reaction temperature increased, due to the gas cooling in the sampling valve. This indicated that the difference was small.

The following results were obtained over the whole series of alloy wires, using 0.15 m. lengths of 2.8×10^{-4} m. diameter wire, as described in Chapter 2. Unless otherwise stated, alloy compositions are weight percent.

5.2a Pure Palladium Wire:

The results for pure palladium wire have already been described in Chapter 3. The reaction in the region of $0^{\circ}C$, gives a simple hydrogenation of DMA almost entirely to cis-but-2-ene, until the DMA has been entirely reacted. At this point a rapid isomerisation of the butene occurs to give the thermodynamic distribution of butenes. This is accompanied by a slower hydrogenation of the butenes to butane.

For the results of the Arrhenius Plot see Chapter 2. These show that:

i) The apparent activation energy = 13.3 k.cal. $mole^{-1}$
= 55.9 k.j. $mole^{-1}$

ii) Frequency Factor = 4.5×10^{35} mole $m^{-2} min.^{-1}$

iii) mean cis/trans = 100

iv) Selectivity coefficient S = 0.99

5.2b 83% Palladium, 17% Gold Alloy Wire:

The results for this alloy gave a very similar picture to that for pure palladium, the only difference being that the reaction temperature was slightly higher.

Temp $^{\circ}C$	Temp $^{\circ}A$	$\frac{I}{T} \times 10^{-3}$ $^{\circ}A^{-1}$	Rate	Log_{10} Rate	S
25	298	.3356	0.096	$\bar{2}.9823$	0.87
43	316	.3165	0.386	$\bar{1}.5866$	0.95
64	337	.2967	1.80	0.2553	0.76
75	348	.2874	3.43	0.5353	0.96
79	352	.2841	5.20	0.7160	0.98

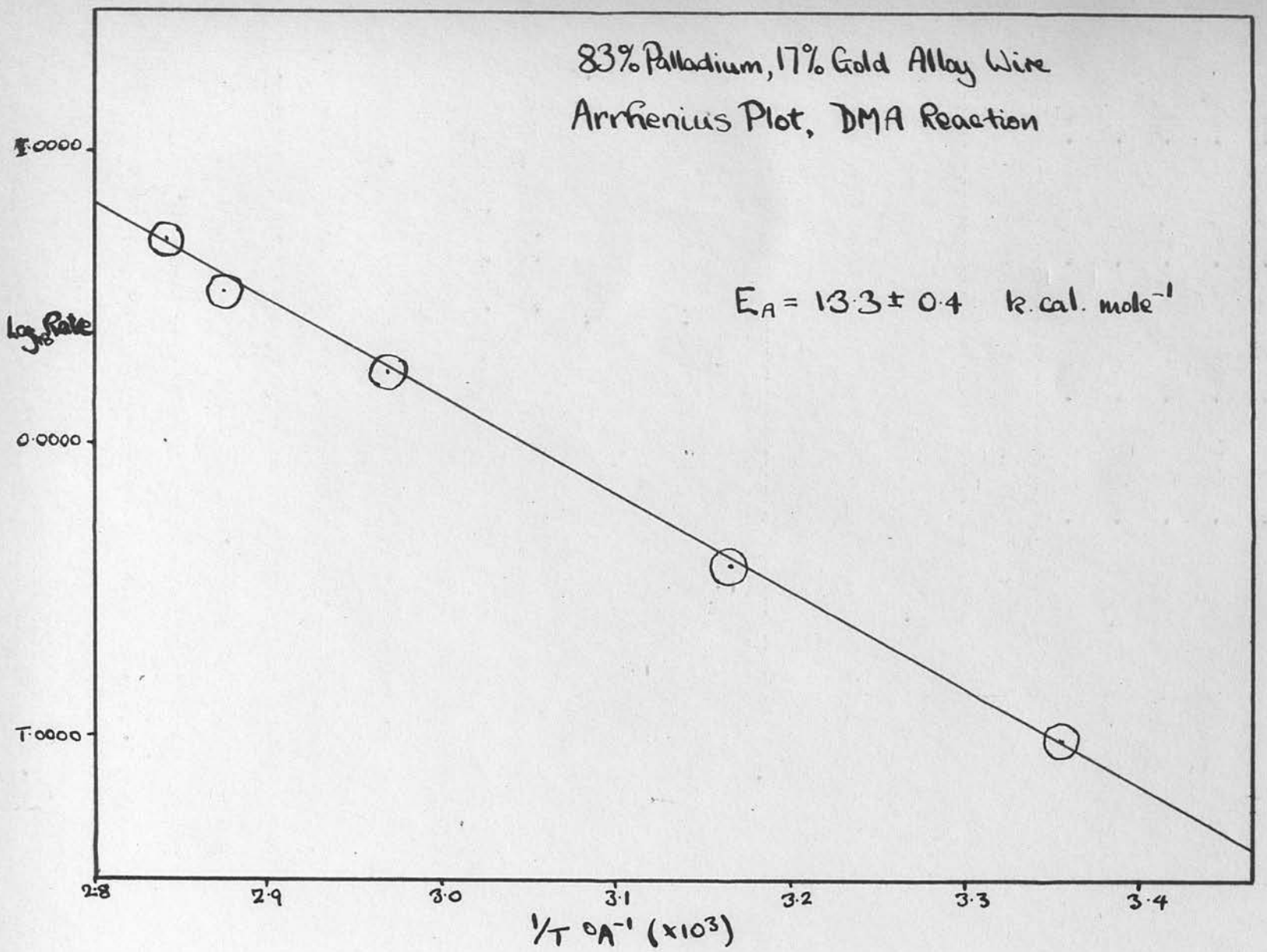

83% Palladium, 17% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
$E_A = 13.3 \pm 0.4$ k.cal. mole^{-1}
1·0000
Log Rate
0·0000
T·0000
2·8
2·9
3·0
3·1
3·2
3·3
3·4
1/T °A^{-1} (x10^3)

Fig 15

The cis/trans ratio was large and rather inconsistent and is not shown here.

This gives the Arrhenius Gradient = 3.0 ± 0.2

$\therefore$ i) The apparent activation energy = 13.7 ± 0.8 k.cal. $mole^{-1}$
= 57.5 ± 3.2 kj. $mole^{-1}$

ii) The frequency factor = 8.8×10^{34} molecules.$m^{2}min^{-1}$

iii) Mean selectivity factor = 0.95

5.2c <u>The 60% Palladium, 40% Gold Alloy Wire:</u>

Temp °C	Temp °A	$\frac{1}{T} \times 10^{-3}$ $°A^{-1}$	Rate $\%min^{-1}$	Log_{10} Rate	cis/trans	S
62	335	2.985	0.225	$\bar{1}.3522$	36.5	0.82
91	364	2.747	1.14	0.0596	42.5	0.96
116	389	2.571	2.83	0.4518	54.5	0.97
118	391	2.558	3.55	0.5502	33.5	0.95
122	395	2.532	5.75	0.7597	36.5	0.93

The anomalous value of S for the run at 62°C is due to but-1-ene produced from the trace of ethyl acetylene, and to cut-off in the integrator affecting the low numbers involved more than usual.

Arrhenius Gradient = 3.03 ± 0.2

$\therefore$ i) Apparent activation energy = 14.0 ± 1.2 k.cal.$mole^{-1}$
= 58.8 ± 5.0 kj.$mole^{-1}$

ii) Frequency Factor = 5.1×10^{34} molecules,m^{-2},min^{-1}

iii) cis/trans 37

iv) Mean selectivity factor = 0.96

5.2d/

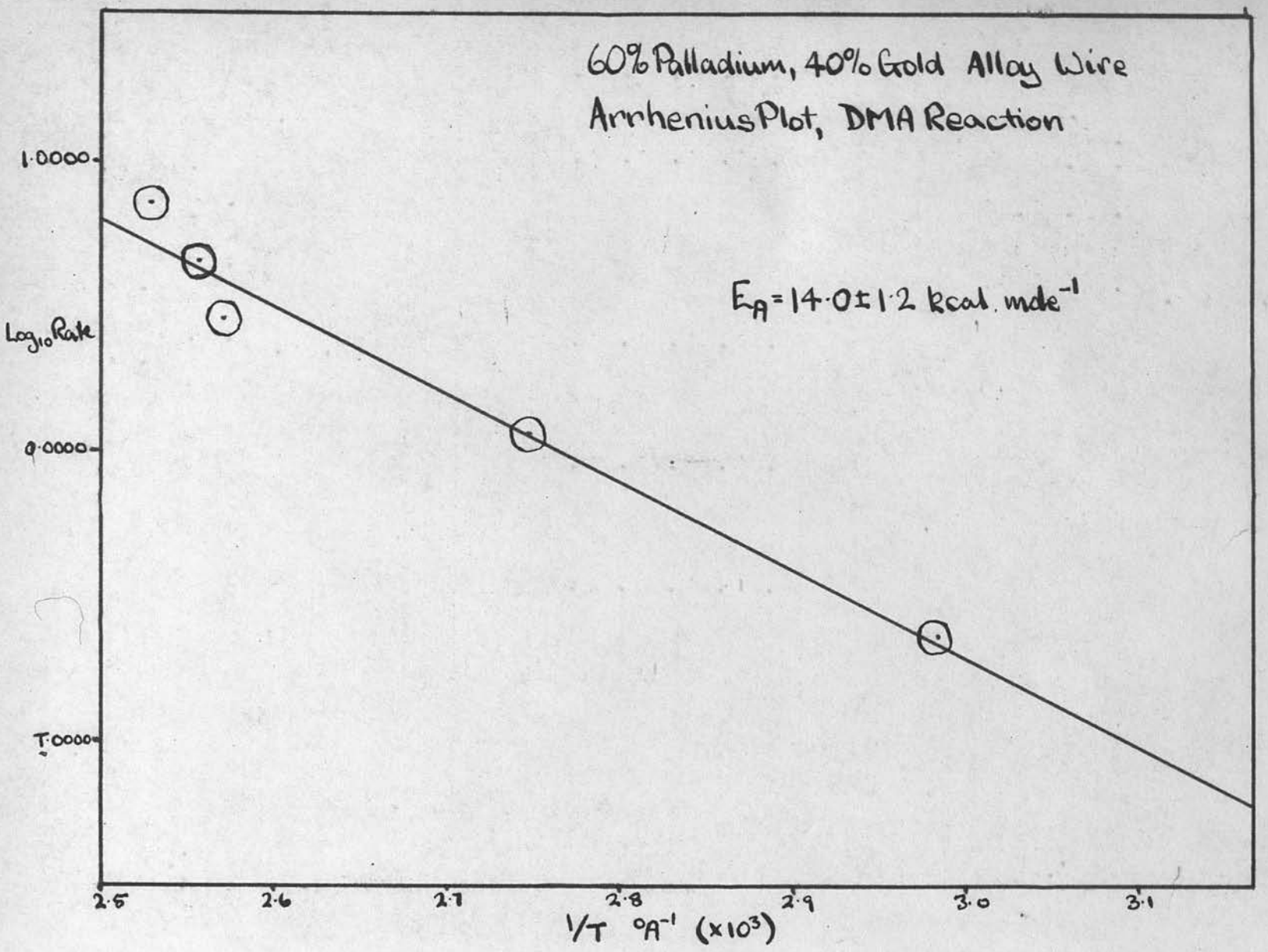

60% Palladium, 40% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
$E_A = 14.0 \pm 1.2$ kcal. mole^{-1}
1.0000
0.0000
-1.0000
Log_{10} Rate
2.5
2.6
2.7
2.8
2.9
3.0
3.1
1/T °A^{-1} (x10^3)

Fig 16

5.2d The 40% Palladium, 60% Gold Alloy Wire:

This alloy was again very similar and appeared to be active in a very similar region of temperature to the 60:40 Alloy.

Temp ^{o}C	Temp ^{o}A	$\frac{1}{T} {}^{o}A^{-1} \times 10^{-3}$	Rate	Log_{10} Rate	Cis/trans	S
49	322	3.110	0.13	$\bar{1}.1139$	28.1	0.91
52	325	3.068	0.17	$\bar{1}.2304$	33.5	0.93
92	365	2.740	1.46	0.1644	31.7	0.96
100	373	2.681	2.93	0.4664	44.5	0.96
110	383	2.611	3.43	0.5353	42.5	0.96
120	393	2.545	10.5	1.0212	14.7	0.92

Arrhenius Gradient = 3.02 ± 0.1

$\therefore$ i) Apparent Activation Energy = 13.9 ± 0.5 k.cal.mole^{-1}

ii) Frequency Factor = 1.71×10^{34} molecules m^{-2},min^{-1}

iii) Cis/trans 35

iv) Mean selectivity factor = 0.94

5.2e The 26% Palladium, 74% Gold Alloy Wire:

This alloy began to show changes, although still very similar. The zero order profile began to show distinct signs of self poisoning and the proportion of minor products began to grow.

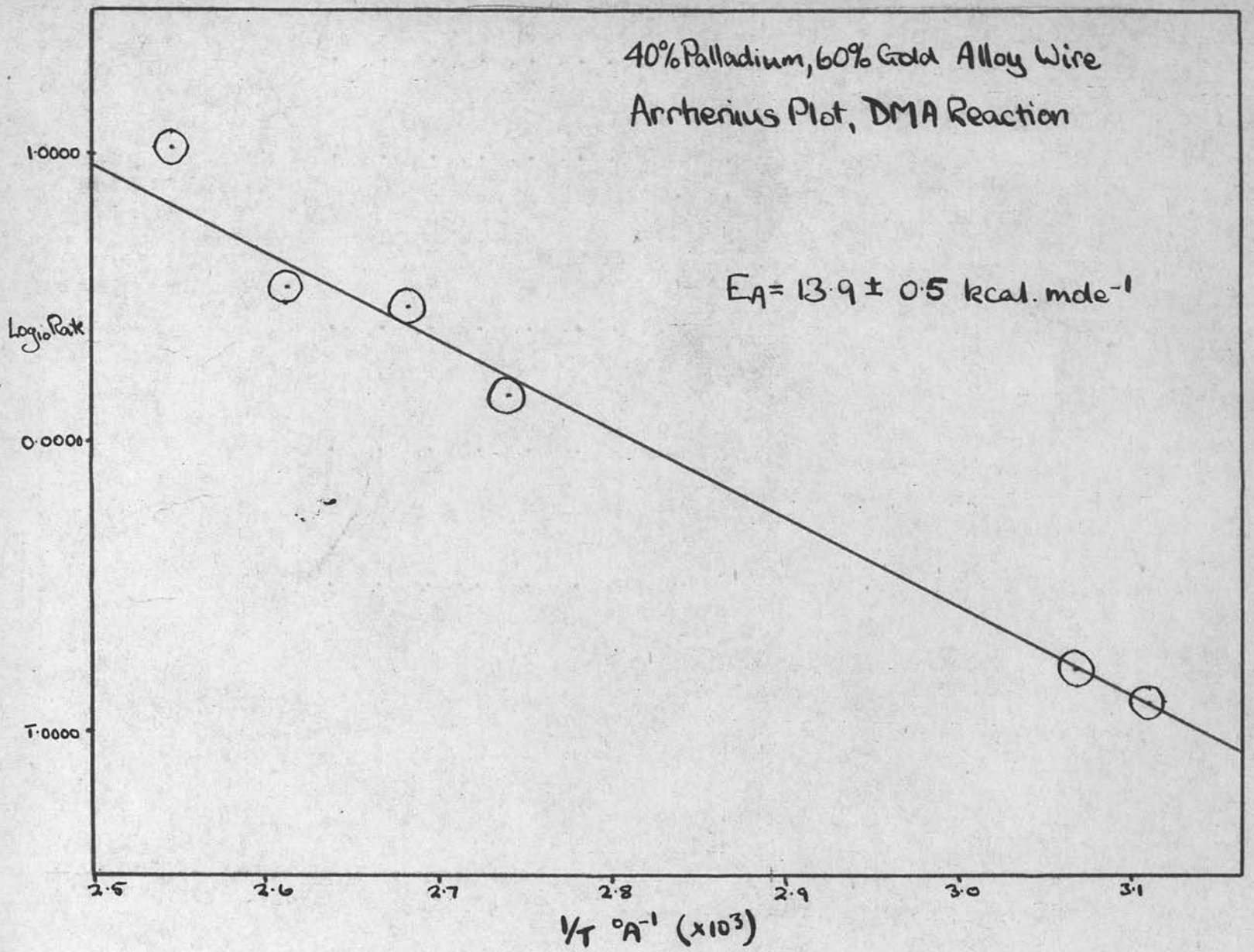

40% Palladium, 60% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
$E_A = 13.9 \pm 0.5$ kcal. mole^{-1}
Log$_{10}$ Rate
1·0000
0·0000
T·0000
2·5
2·6
2·7
2·8
2·9
3·0
3·1
1/T °A^{-1} (x10^3)

Fig 17.

Temp °C	Temp °A	$\frac{1}{T}$ $^{\circ}A^{-1}$ x 10^3	Rate	Log_{10} Rate	Cis/trans	S
115	385	2.597	0.44	$\bar{1}.6435$	31.3	0.94
145	418	2.392	1.44	0.584	22.7	0.92
163	436	2.294	2.55	0.4065	28.5	0.97
166	439	2.278	2.30	0.3617	20.0	0.92
168	441	2.268	3.18	0.5024	22.5	0.93
170	443	2.257	3.55	0.5502	16.8	0.92
175	448	2.232	4.00	0.6021	17.0	0.91

The cis/trans ratio shows a decline as the temperature rises, the change in S is not so marked.

Arrhenius Gradient = 2.92 ± 0.2

$\therefore$ i) Apparent Activation Energy = 13.4 ± 0.9 k.cal. $mole^{-1}$

= 56.2 ± 2.8 k.j. $mole^{-1}$

ii) Frequency Factor = 6.18×10^{32} molecules m^{-2} min^{-1}.

iii) cis/trans (mean) = 22

iv) Mean selectivity factor = 0.93

5.2f <u>The 18.5% Palladium, 81.5% Gold Alloy Wire</u>:

This alloy was very similar in properties to the 26:74 alloy described in 5.2e except that the temperature range was raised by some 25°C. It proved impossible to get any reproducible rates at the lower end of the range.

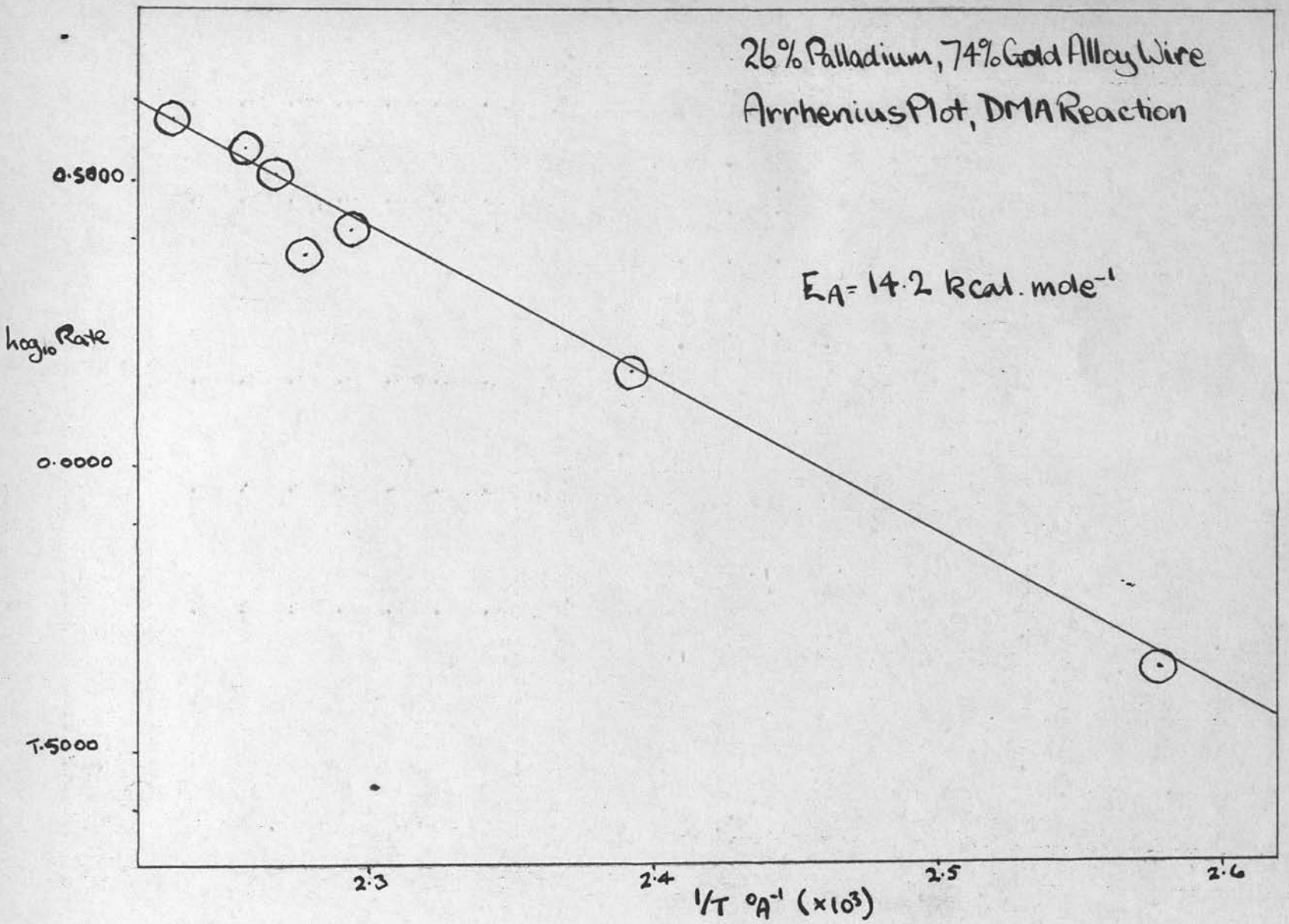

26% Palladium, 74% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
E_A = 14.2 kcal. mole^{-1}
0.5000
0.0000
T.5000
$\log_{10}$ Rate
2·3
2·4
2·5
2·6
1/T °A^{-1} (×10^3)

Fig 18

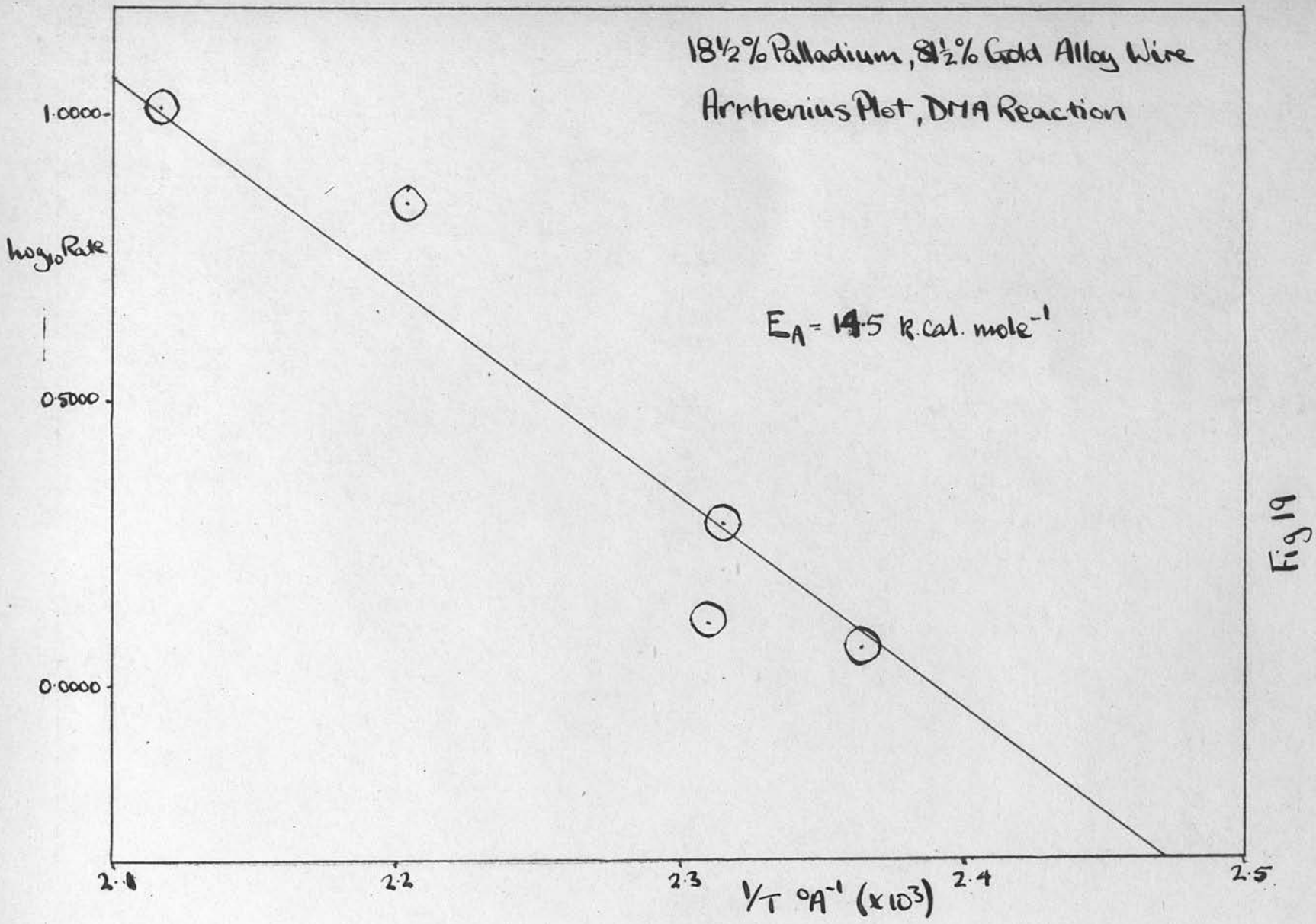

18½% Palladium, 81½% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
E_A = 14.5 K.cal. mole^{-1}
log$_{10}$ Rate
1·0000
0·5000
0·0000
2·1
2·2
2·3
2·4
2·5
1/T °A^{-1} (x10^3)

Fig 19

Temp °C	Temp °A	$\frac{1}{T}$ $^{\circ}A^{-1}$ x 10^{-3}	Rate	Log_{10} Rate	Cis/trans	S
150	423	2.364	1.16	0.0645	13.8	0.91
159	432	2.314	1.95	0.2900	20.4	0.92
160	433	2.309	1.27	0.1038	15.6	0.90
181	454	2.203	1.95	0.8420	15.7	0.90
202	475	2.116	11.5	0.0607	10.9	0.86

Arrhenius' Gradient = 2.92 ± 0.4

$\therefore$ i) Apparent Activation Energy = 13.4 ± 2.4 k.cals. $mole^{-1}$

= 56.2 ± 10.1 k.j. $mole^{-1}$

ii) Frequency Factor = 2.8×10^{32} molecules m^{-2} min^{-1}

iii) Cis/trans = 15.6

iv) Mean selectivity factor = 0.90

5.2g <u>The 9% Palladium, 91% Gold Alloy Wire</u>:

This proved to be a very difficult alloy to deal with possibly due to the small number of sites available for reaction and the high temperature. Certainly the reaction was now markedly self-poisoning and the temperature range showed a large increase.

Owing to circumstances, the runs quoted here were carried out, in some cases, at relatively long time intervals. The results obtained fall into two groups, separated by a factor of about four; i.e. at a given temperature the reaction rate in one case is about four times that of the other. The disparity can be connected with the time intervals mentioned/

mentioned above. Obviously some factor in the reaction had changed but both sets of results give a similar activation energy.

Temp °C	Temp °A	$\frac{1}{T} \times 10^{-3}$ $°A^{-1}$	Rate	Log_{10} Rate	Cis/trans	S
199	472	2.119	0.132	$\bar{1}.1206$	17.1	0.89
215	488	2.049	1.18	0.0719	9.9	0.84
225	498	2.008	0.440	$\bar{1}.6435$	7.5	0.79
240	513	1.949	0.480	$\bar{1}.6812$	4.8	0.72
246	519	1.927	1.30	0.1139	14.4	0.88
355	528	1.894	5.00	0.6990	10.0	0.84
260	533	1.876	5.15	0.7118	8.7	0.84

Arrhenius Gradients = a) 3.5 ± 0.4
b) 3.1 ± 0.4

$\therefore$ i) Apparent activation energies = a) 16.5 ± 2.5 k.cals $mole^{-1}$
b) 14.2 ± 2.5 k.cals $mole^{-1}$
= a) 69.3 ± 10.5 k.j. $mole^{-1}$
b) 59.6 ± 10.5 k.j. $mole^{-1}$

ii) Frequency Factors = a) 5.93×10^{32} molecules, $m^{-2} min^{-1}$
b) 5.95×10^{31} molecules, m^{-2}, min^{-1}

iii) Cis/trans = a) 9.5
b) 9.8

iv) Mean selectivity Factors a) 0.84
b) 0.80

The (a) series, which was the more active, shows much less variation of cis/trans and S, indicating possibly that the difference between it and (b) was a shorter lifetime for surface species.

5.2h <u>The 6% Palladium, 94% Gold Alloy Wire</u>:

This once more proved to be a very difficult catalyst to deal with. The/

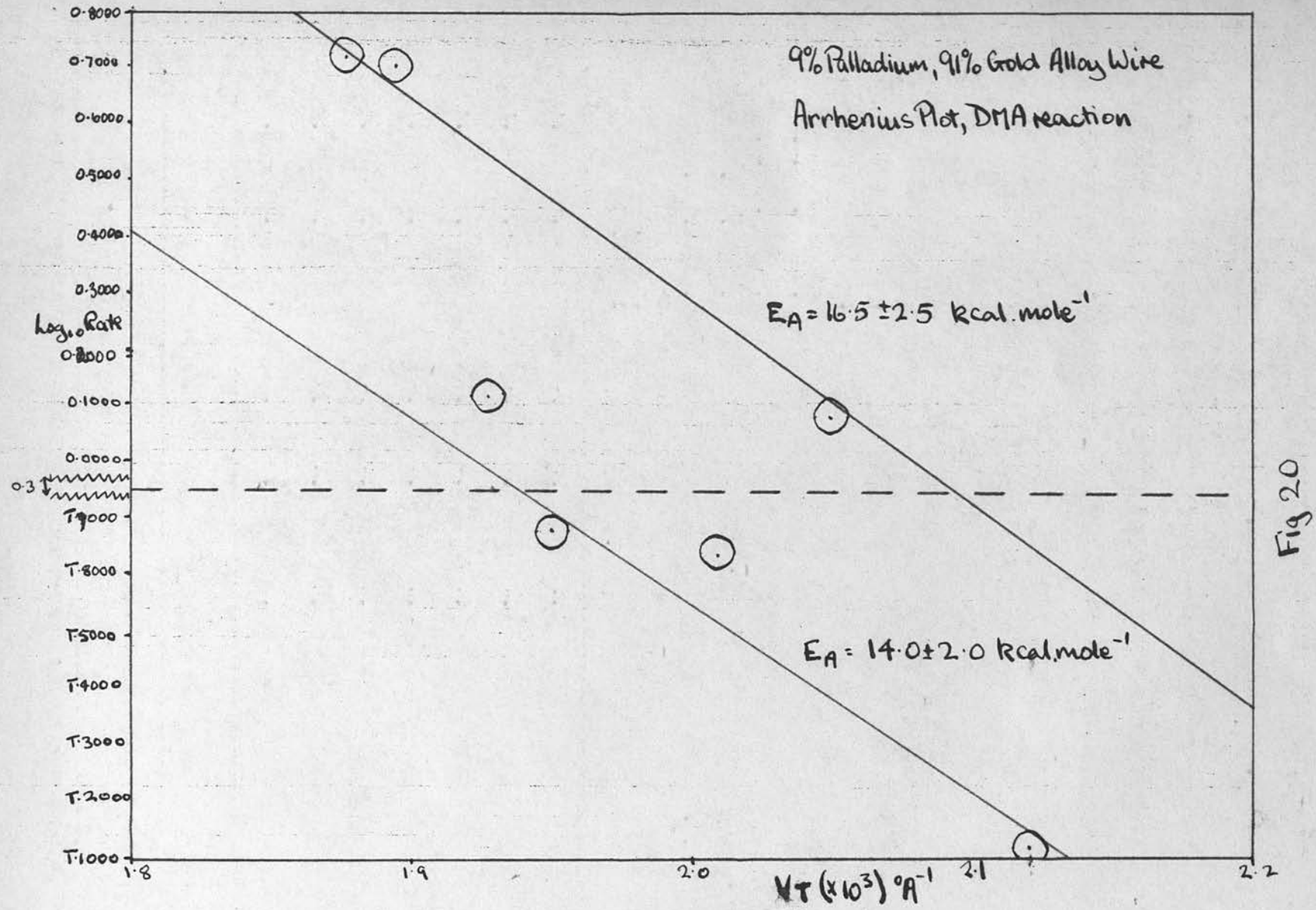

9% Palladium, 91% Gold Alloy Wire
Arrhenius Plot, DMA reaction
$E_A = 16.5 \pm 2.5$ kcal.mole^{-1}
$E_A = 14.0 \pm 2.0$ kcal.mole^{-1}
Log$_{10}$ Rate
0·8000
0·7000
0·6000
0·5000
0·4000
0·3000
0·2000
0·1000
0·0000
0·3
T·9000
T·8000
T·5000
T·4000
T·3000
T·2000
T·1000
1·8
1·9
2·0
2·1
2·2
$\frac{1}{T}$ ($\times 10^3$) °A^{-1}

Fig 20

The temperature range was very high, and only a few fast reactions showed any signs of reproducibility. These are quoted below:

Temp °C	Temp °A	$\frac{1}{T} \times 10^3$ $^{\circ}A^{-1}$	Rate	Log_{10} Rate	Cis/trans	S
270	543	1.842	0.388	$\bar{1}.5888$	5.2	0.73
276	549	1.821	1.18	0.1055	5.3	0.76
276	549	1.821	1.30	0.1139	7.9	0.82
284	557	1.795	1.15	0.0607	4.5	0.73
295	568	1.761	1.61	0.2068	5.9	0.75
300	573	1.745	2.75	0.4393	4.2	0.71

Arrhenius Gradient = 3.05 ± 0.7

$\therefore$ i) Apparent activation energy = 14.0 ± 2.9 k.cals.mole^{-1}

= 58.8 ± 12.2 k.j. mole^{-1}

ii) Frequency Factor = 1.68×10^{31} molecules, m^{-2},min^{-1}

iii) Cis/trans = 5.5

iv) Mean selectivity factor = 0.75

5.2i <u>The 3.5% Palladium, 96.5% Gold Alloy Wire</u>:

The properties of this catalyst were quite different. It seemed to exhibit a maximum in activity as the reaction temperature was raised. It also poisoned very rapidly, which made rate measurements rather subjective. In fact, the rate seemed to vary very little below 335°C and then began to fall off.

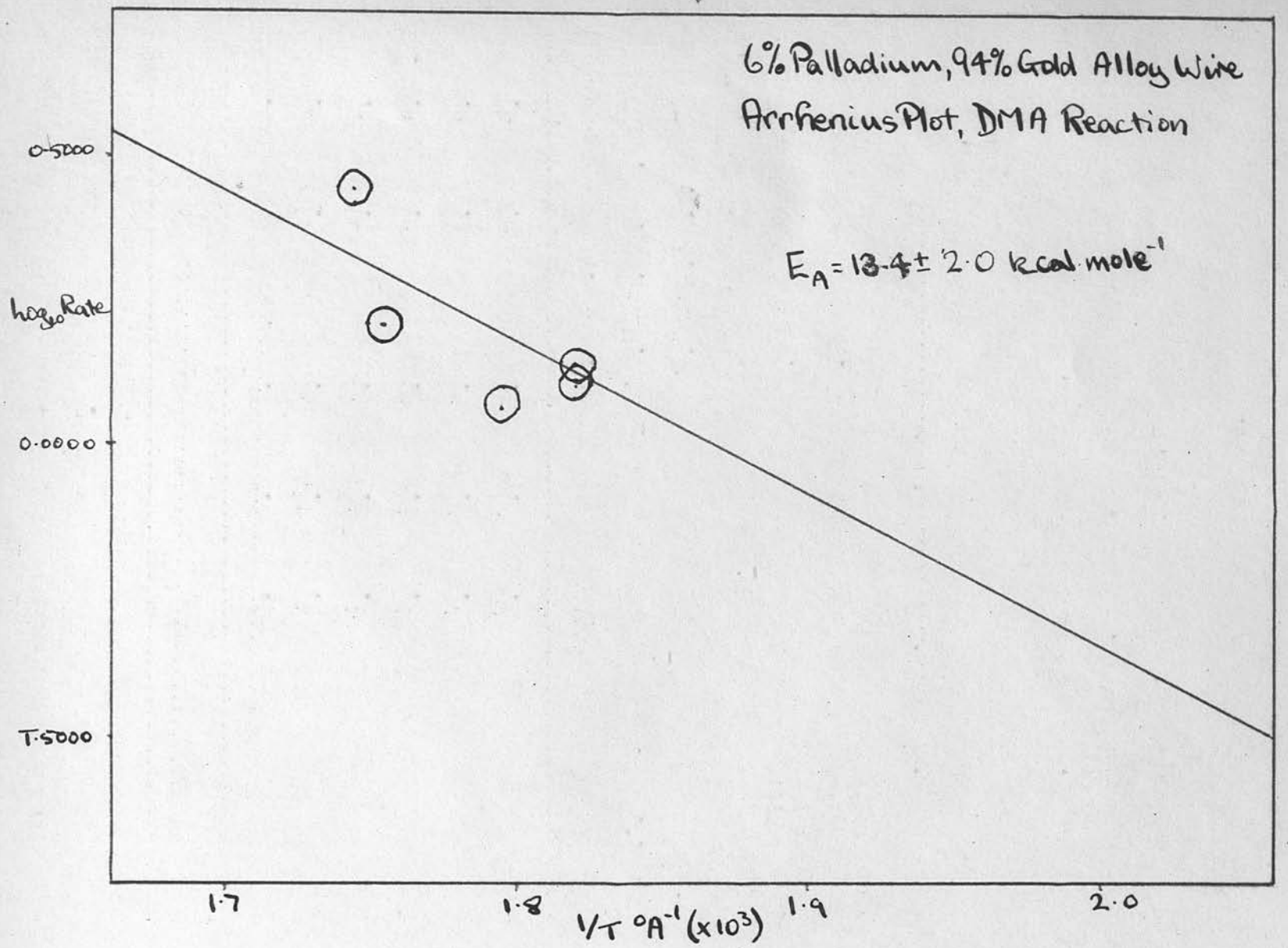

6% Palladium, 94% Gold Alloy Wire
Arrhenius Plot, DMA Reaction
$E_A = 13.4 \pm 2.0$ kcal mole^{-1}
0·5000
log$_{10}$ Rate
0·0000
T·5000
1·7
1·8
1·9
2·0
1/T °A^{-1} (x10^3)

Fig 21

Temp °C	Temp °A	Approx. Init. Rate	Cis/trans	S	% age 1,3 diene @ 30 mins	Max. DMA* Conversion %
314	587	1.25	5.7	0.78	2.5	25
325	598	1.30	4.6	0.74	2.4	25
332	605	1.40	3.6	0.71	3.0	30
338	611	0.44	4.2	0.73	1.2	15
347	620	0.38	4.2	0.72	1.5	15

* Including Isomerisation.

Traces of methyl allene and methyl acetylene occurred. This pattern is very reminiscent of the low temperature reaction on pure gold wires, with the rapid burst of almost "superactivity" which seems to be rapidly self poisoning.

i) Cis/trans = 4.4

ii) Mean selectivity factor= 0.73

5.2j <u>The 1.5% Palladium, 98.5% Gold Alloy Wire</u>:

Temp °C	Temp °A	Rate	Cis/trans	S	% age 1,3 diene @ 30 mins	Max. DMA Conversion %
324	597	0.83	4.0	0.73	2.05	25
339	612	0.90	4.5	0.74	3.00	35
350	623	0.58	3.4	0.70	2.5	20
366	639	0.19	4.2	0.73	0.7	15

Traces/

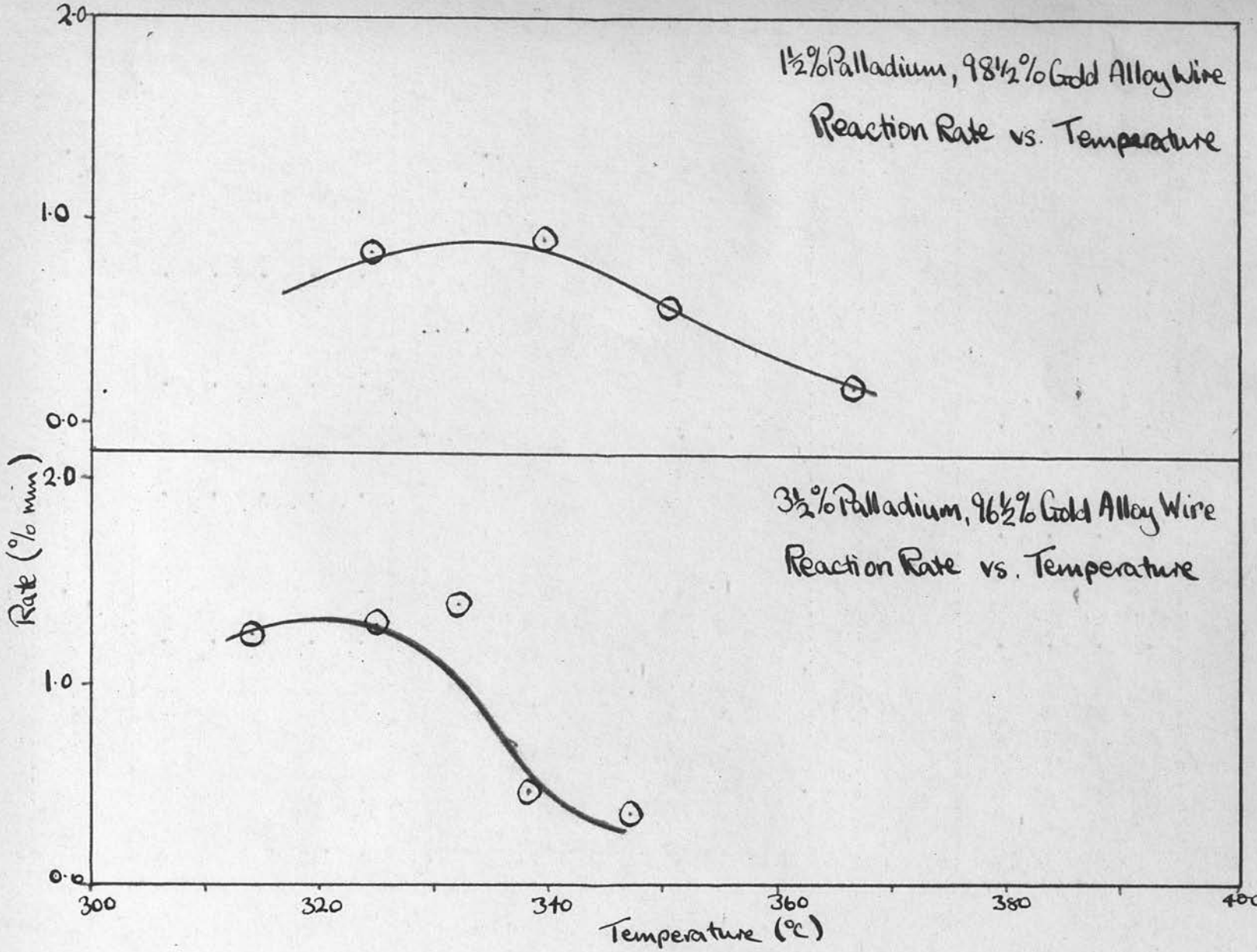

1½% Palladium, 98½% Gold Alloy Wire
Reaction Rate vs. Temperature
2·0
1·0
0·0
3½% Palladium, 96½% Gold Alloy Wire
Reaction Rate vs. Temperature
2·0
1·0
0·0
Rate (% min)
300
320
340
360
380
400
Temperature (°C)

Fig 22

Traces of methyl allene, methyl acetylene and propylene occurred.

i) cis/trans = 4.1

ii) Mean selectivity factor = 0.72

As expected this alloy was very similar to gold.

5.2k Summary of Results:

Alloy Comp. Pd:Au Atom %	Alloy Comp. Pd:Au Weight %	Apparent Activn. Energy $k.j.\ mole^{-1}$	Frequency Factor*	Cis/trans	S	Temp at which rate= 1% min^{-1}
100:0	100:0	55.9	4.5×10^{35}	100	0.99	-5°C
91:9	83:17	57.5	8.8×10^{34}	85	0.95	52°C
75:25	60:40	58.8	5.1×10^{34}	37	0.96	69°C
55:45	40:60	58.3	1.71×10^{34}	35	0.94	83°C
40:60	26:74	56.2	6.18×10^{32}	22	0.93	137°C
30:70	18.5:81.5	56.2	2.8×10^{32}	15.6	0.90	156°C
15:85	9:91	69.3 59.6	5.93×10^{31}	9.7	0.82	227°C
10:90	6:94	58.8	1.68×10^{31}	5.5	0.74	265°C
6:94	3.5:96.5	-	-	4.4	0.73	310°C
3:97	1.5:98.5	-	-	4.1	0.72	330°C

The general trends thus illustrated are the lack of variation in the experimental values for the apparent activation energy, which are identical within experimental error. The general fall in frequency factor cis/trans ratio and "s" were all to be expected, the latter two on thermodynamic grounds, if on no other.

* In molecules, min^{-1}, m^{-2}.

5.21/

5.21 Other Observations:

i) Isomerisation of Dimethyl Acetylene:

Traces of 1,3 butadiene were noted from the 60:40 alloy onwards but it was not until the 9:91 alloy was reached that the concentration in the gas phase rose above the trace level. Even smaller quantities of methyl allene (1,2 butadiene) were noted from the 18.5:81.5 alloy onwards. For both isomers only the three most gold rich alloys produced significant quantities in the gas phase.

ii) Carbon Loss:

Generally carbon loss seemed to be low, except in one region, that covered by the 40:60, 26:74, 18.5:81.5 alloys, in which considerable loss occurred with perhaps as much as 20% of the carbon apparently vanishing. The actual loss was difficult to determine, as sample sizes from the Perkin Elmer sampling valve were variable. The general trend would indicate though, that on these catalysts, between 10 and 20% of the carbon vanished. In this region, however, considerable deposition of polymerised material on the reaction vessel walls was noted, which would account for the loss. The polymer produced was solid, hard and clear, only showing up after treatment with nitric acid had carbonised the surface. It is tempting to suppose that this polymerisation occurs via adsorbed 1,3 butadiene, which is known to polymerise very readily. This would suppose that considerable quantities of 1,3 butadiene are formed on the surface, and that most of it ends up as polymer. That this polymerisation begins to decrease as the temperature rises, is not really surprising, rising temperature would mean a shorter probable surface lifetime for the adsorbed/

adsorbed species and the increase in the amount of available energy favours desorption rather than polymerisation. Possibly also the catalyst is a factor in this, i.e. specific active sites may be needed to trigger the polymerisation, these presumably grow less in number as the concentration of palladium decreases. At low temperatures, with palladium rich catalysts, presumably hydrogenation of the DMA; as opposed to polymerisation and isomerisation, is important.

iii) Reaction Profile:

The profile of the disappearance of DMA is not without interest and it may conveniently be divided into three parts,

a) A very slow "warm up" period. This tends to get shorter as the temperature and gold concentration increase, vanishing completely at very high gold concentrations. It seems probable that this is due to the need for equilibration of the surface species. Presumably hydrogen is adsorbed more quickly than the DMA, thus there is a need for DMA to "catch up" with the hydrogen coverage.

Hydrogen is a poison for DMA hydrogenation, thus the coverage of DMA not only has to catch up, but has to remove the excess hydrogen which is, at the same time, hindering its ability to do so. Some reactions, particularly those at lower temperatures, never get past the "warm up" stage, presumably because the DMA never does manage to overcome the hydrogen poisoning; i.e. the wire was not thoroughly degassed.

b)/

b) The zero order stage of the reaction. This usually covers most of the DMA disappearance. Beginning at well over 90% DMA it covers the reaction down to 2 or 3% DMA for all except the alloys containing 74% or more of gold.

c) The final stage. Poisoning begins to set in at higher gold contents and temperatures. This stage is unimportant in palladium rich alloys but becomes very important at 74% or more of gold, when serious poisoning occurs. At very high gold contents the reaction is literally stopped and in some cases the reaction profile shows a continuously decelerating curve. This is probably due to strongly adsorbed dehydrogenated species, or to high polymers on the surface.

iv) The Pure Palladium Wire Result:

The experimental frequency factor of 100% palladium wire, differs from that which might be expected by comparison with the other results by a factor of ten or so. One effect to which this may be attributed is that because of the historical development of this work, palladium was activated in a more robust fashion than the alloys. This could mean that the wire was perhaps cleaner, and that also a greater portion of its area was in fact cleaned.

Another effect is that of surface area; Gerberich et al (105) and McKee (95) have noted a decline in the surface area of palladium gold alloys as gold is added, and it seems reasonable to suppose the addition of gold will markedly change the ability of the surface to anneal. The surface tension of palladium being twice that of gold (1500 dyne/cm to 754 dyne/cm).

CHAPTER 6.

DISCUSSION

6.1 The Selectivity of the Alloy Catalysts

From the point of view of both the cis/trans ratio and the selectivity factor (s), the selectivity of the alloys for cis-but-2-ene as product decreases with the concentration of palladium. Whether this is due to any inherent change in the catalyst kinetics or is simply due to thermodynamics is hard to say. Certainly, on balance, the rise in reaction temperature must be considered as a major factor, since presumably the reaction to produce a surface species which will result in other products than cis-but-2-ene, has a higher activation energy than the normal reaction. Thus rises in temperature will tend to favour the side reactions. It must be remembered however, that gold can be an efficient isomerisation catalyst, and it is possible that as the concentration of surface palladium decreases, isomerisation may occur on sites not active enough for the initial hydrogenation. Temperature must, however, be considered as the main factor. The production of traces of butane, probably occurs during the initial visit of the DMA to the catalyst surface, involving perhaps very active surface sites. It seems unlikely that it occurs because of subsequent visits to the surface of butene molecules while there are still appreciable quantities of DMA. For the high gold concentration alloys selectivity tends to drop slightly as poisoning sets in. This is probably because less active sites will poison more slowly and it is on these "slow" sites that isomerisation of the half hydrogenated state might be expected to occur.

6.2/

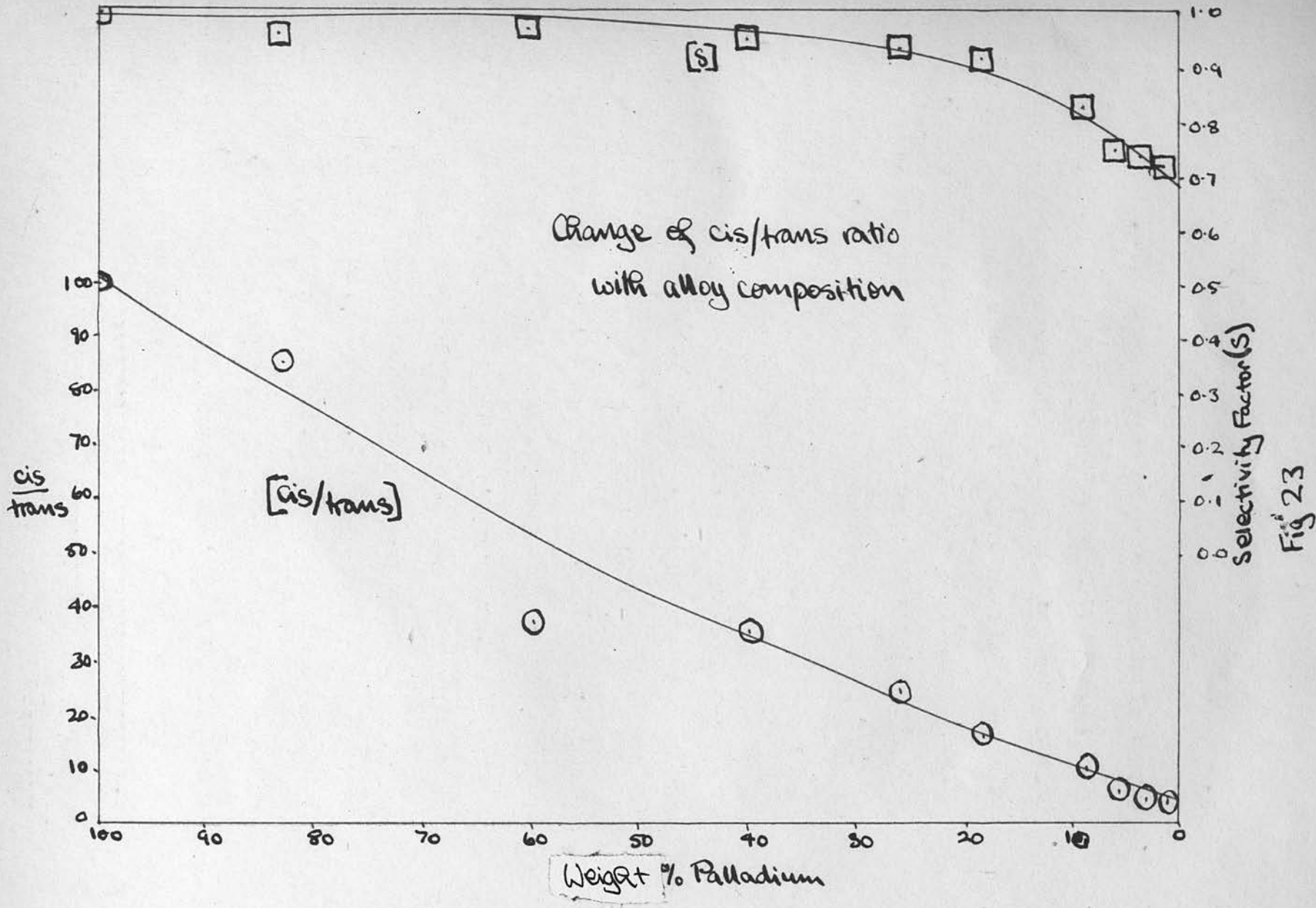

Change of cis/trans ratio
with alloy composition
[S]
[cis/trans]
cis / trans
Selectivity Factor(S)
Weight % Palladium
100
90
80
70
60
50
40
30
20
10
0
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0

Fig 23

6.2 The Arrhenius Plot Results:

These are the most obviously surprising results obtained, the invariance of the apparent activation energy for DMA hydrogenation over the whole alloy series being entirely unexpected. The inferences from this fact is very important. It suggests that the process is independant of the changes in bulk properties of the alloy series; i.e. it is unaffected by changes in geometry, d-band vacancy, or Fermi Level. It must therefore depend on some property which remains unchanged over the entire series but there are no obvious properties of the bulk system, of which this can be said, and which are also of interest catalytically. The obvious answer then is that the process depends on some property connected solely with the active surface sites. The immediately obvious answer is that palladium atoms form the active sites on all the alloys and that quite possibly islands of palladium atoms may be the sites.

Since the apparent activation energies are all very similar, then a comparison of the frequency factors of the alloys is particularly significant and should give a good indication of the relative concentration of active sites over the alloy series.

The table of results for the alloys shows the experimental results, which exhibit the expected decline in frequency factor with the decrease in palladium concentration. If, as proposed, the active sites are islands of palladium atoms on the catalyst surface, then the frequency factors and the calculated probabilities of such islands occurring should be related.

6.3/

6.3 The Calculation of the Probabilities of Islands of Palladium Atoms Occurring on the Alloy Surfaces:

The palladium-gold alloys form a f.c.c. crystal system which means that on the 100 face, each atom has four nearest neighbours, Assuming that this is true on the alloy surface, then it is possible to calculate the probability of a particular atom being palladium and the probabilities that the four surrounding atoms contain one, two, three or four palladium atoms, i.e. forming islands of two, three, four or five palladium atoms.

Let the probability that a particular surface atom is palladium = x

$\therefore$ Proby Pd atom surrounded by 4Pds = x^5

" " " " " 3Pds. 1Au = $4x^4 (1-x)$

" " " " " 2Pds. 2 Aus. = $6x^3 (1-x)^2$

" " " " " 1 Pd. 3 Aus. = $4x^2 (1-x)^3$

" " " " " 4 Aus. = $x (1-x)^4$

By appropriate substitution and summation the probabilities of DMA being adsorbed on a site of 3 or more, or 4 or more, palladium atoms can be calculated. The results for a selection alloys were calculated and tabulated.

Alloy Comp. Atom %	1 adj.Pd.	$\log_{10}$ 1 adj.	2 adj.Pd.	$\log_{10}$ 2 adj.
100:0	1	0.0000	1	0.0000
83:17	0.8293	$\bar{1}$.9188	0.8158	$\bar{1}$.9116
60:40	0.5846	$\bar{1}$.7668	0.4925	$\bar{1}$.6924
40:60	0.3482	$\bar{1}$.5419	0.2099	$\bar{1}$.3220
26:70	0.1820	$\bar{1}$.2601	0.0725	$\bar{2}$.8601
18.5:81.5	0.1034	$\bar{1}$.0145	0.0293	$\bar{2}$.4663
9:91	0.0288	$\bar{2}$.4594	4.41×10^{-3}	$\bar{3}$.6442
6:94	0.0132	$\bar{2}$.1206	1.20×10^{-3}	$\bar{3}$.0774
3.5:96.5	0.0069	$\bar{3}$.8388	2.46×10^{-4}	$\bar{4}$.3903
1.5:98.5	8.80×10^{-4}	$\bar{4}$.9445	1.99×10^{-5}	$\bar{5}$.2989

Alloy	3 adj. Pd.	$\log_{10}$ 3 adj.	4 adj. Pd.	$\log_{10}$ 4 adj.
100:0	1	0.0000	1.	0.0000
83:17	0.7166	$\bar{1}$.8553	0.3939	$\bar{1}$.5944
60:40	0.2851	$\bar{1}$.4550	0.0778	$\bar{2}$.8910
40:60	0.0717	$\bar{2}$.8550	0.0102	$\bar{2}$.0086
26:70	0.0147	$\bar{2}$.1676	1.19×10^{-3}	$\bar{3}$.0755
18.5:81.5	4.03×10^{-3}	$\bar{3}$.6058	2.17×10^{-4}	$\bar{4}$.3365
9:91	2.45×10^{-4}	$\bar{4}$.3886	5.91×10^{-6}	$\bar{6}$.7716
6:94	4.95×10^{-5}	$\bar{5}$.6947	7.78×10^{-7}	$\bar{7}$.8910
3.5:96.5	6.02×10^{-6}	$\bar{6}$.7796	5.25×10^{-8}	$\bar{8}$.7202
1.5:98.5	2.03×10^{-7}	$\bar{7}$.3075	8×10^{-10}	$\bar{10}$.9031

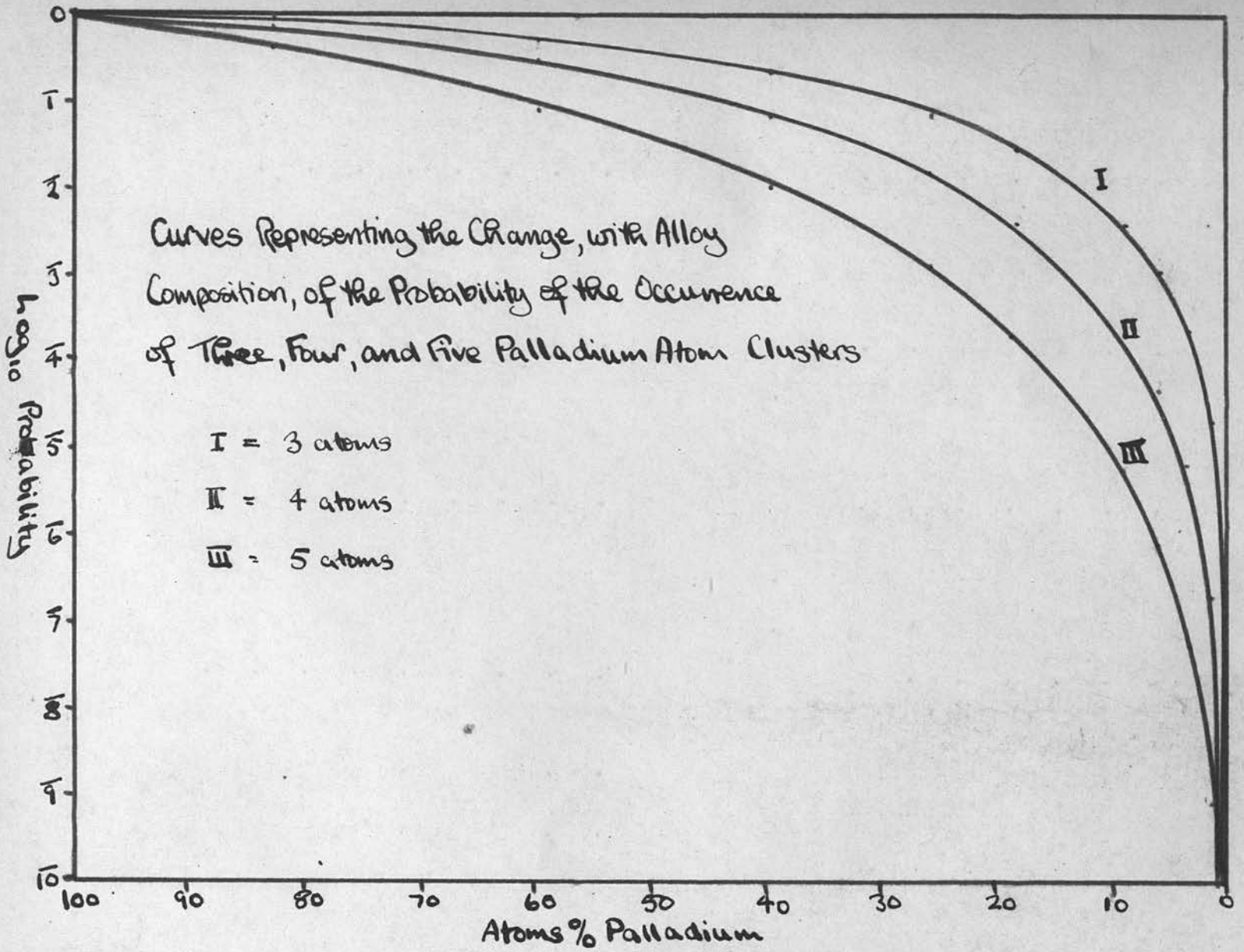

Curves Representing the Change, with Alloy Composition, of the Probability of the Occurrence of Three, Four, and Five Palladium Atom Clusters
I = 3 atoms
II = 4 atoms
III = 5 atoms
I
II
III
Log. Probability
0
1/10
2/10
3/10
4/10
5/10
6/10
7/10
8/10
9/10
10/10
100
90
80
70
60
50
40
30
20
10
0
Atoms % Palladium

Fig 24

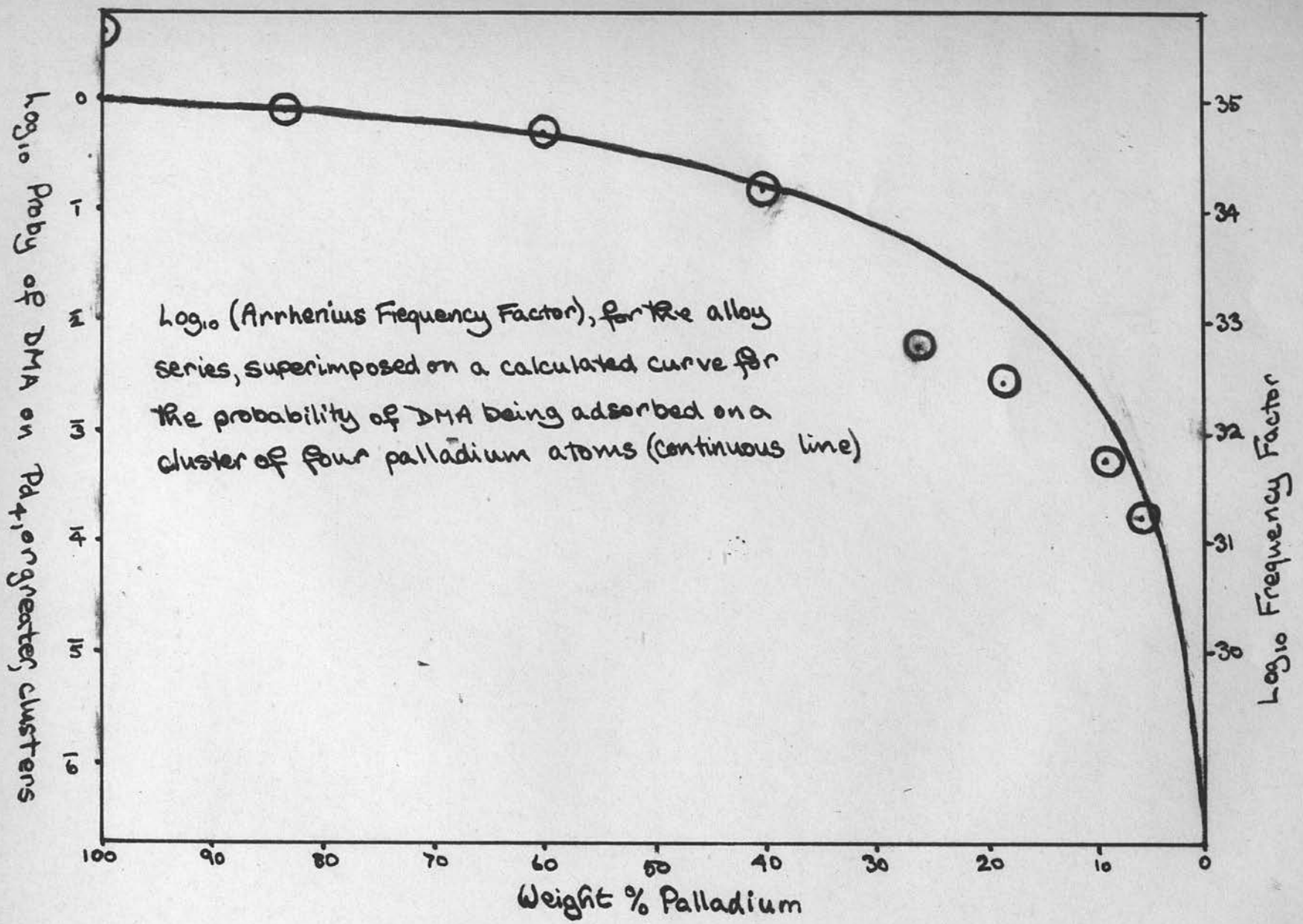
These results were graphed in the form $\log_{10}$ proby., v.s. alloy composition. It was found that the curve obtained for the probability of the occurrence of three adjacent palladium atoms, to an initial palladium atom, i.e. an island of four or more palladium atoms was almost identical to that obtained from plotting $\log_{10}$ Frequency Factor v.s. alloy composition.

This indicates that FOUR adjacent palladium atoms are required for an active site to hydrogenate DMA. This is very interesting, since it seems likely that an adsorbed DMA molecule would require two of the palladium atoms for stable adsorption, leaving two available for hydrogen. This would imply that:

i) The reaction is unlikely to involve a physically adsorbed hydrogenation which might well only require one palladium atom to give the necessary hydrogen intermediate.

ii) Since the reaction probably involves atomic hydrogen, then the hydrogen atoms must be relatively immobile on the surface, and a hydrogen molecule must be chemisorbed, in close proximity to the DMA molecule, as atoms. If the idea that palladium islands are necessary to the reaction, is accepted, then so must the implication that in the course of the reaction DMA and hydrogen molecules are simply chemisorbed in close proximity and react. If a DMA molecule is already adsorbed on a four atom island then steric hinderance will probably prevent the adsorption of a similar molecule on the same island.

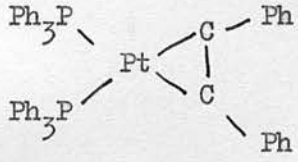
In view of the lack of change in the apparent activation energy, and in view also of the apparent correlation of frequency factor and occurrence of four or more palladium atom islands in the alloy surfaces, these conclusions/


Log10 Frequency Factor
35
34
33
32
31
30
Log10 Prob of DMA on Pd4 or greater clusters
0
-1
-2
-3
-4
-5
-6
100
90
80
70
60
50
40
30
20
10
0
Weight % Palladium
Log10 (Arrhenius Frequency Factor), for the alloy series, superimposed on a calculated curve for the probability of DMA being adsorbed on a cluster of four palladium atoms (continuous line)

conclusions concerning the nature of the reaction must be taken very seriously. The results cannot be adequately explained in terms of the bulk properties of the alloys.

6.4 Acetylene Complexes:

In organometallic chemistry the existance of many complexes incorporating alkyne ligands with transition metals is known. Compounds such as Diphenyl Acetylenes seem particularly able to form the necessary linkages and such compounds as the planar species.



These are well characterised and quite stable. Similar palladium compounds are known to occur but strong electron withdrawing groups, such as ester groups, must be attached to the acetylenic carbons before they achieve any measure of stability (139), but they are known and characterised.

The infra-red spectra of these compounds are interesting and show a reduction of the acetylene stretching peak, from 2200 cm^{-1} to 1760 $cm.^{-1}$, indicating a pronounced weakening of the acetylene bond. It is suggested that the metal-ligand bond involves π-bond donation from the acetylene bond to form a p-π bond with the metal.

That palladium-acetylene linkages are known at all indicates that palladium and alkynes are capable of forming bonds which are probably very strong with respect to most types of surface adsorption.

6.5/

6.5 A Possible Mechanism for the Hydrogenation of Dimethyl Acetylene on Palladium-Gold Alloys:

In discussing a mechanism for the hydrogenation of DMA on palladium gold alloys, the following points must be considered:

i) It is probable that surface clusters of four or more palladium atoms are involved.

ii) If this is so, then hydrogen atoms cannot be mobile between groups of palladium atoms, since then groups of two might be making a contribution; i.e. hydrogen atom from a group of two palladiums could migrate to DMA adsorbed on a group of three palladiums.

iii) Palladium can form fairly stable linkages with alkyne bonds in organometallic compounds.

iv) Gold does not form such linkages: the heat of adsorption of acetylene on gold is only some 88 k.j. $mole^{-1}$, not much more than some values for physical adsorption. In view of (iii) the value for palladium will be very much higher.

v) The apparent activation energy of the reaction does not change over the range of alloys, while the value obtained over gold films (which will be well annealed) is only some 75% of this value.

vi) Palladium is a very strong hydrogenation catalyst, able to chemisorb hydrogen in large quantities, at low temperatures while the comparative activity of gold as a hydrogenation catalyst is very slight.

vii)/

vii) Other research on palladium-gold alloy catalysts (see Chapter 1) has usually indicated a relation between catalytic activity and the bulk electronic properties of the alloys. Gerberich et al (105) have suggested, however, that palladium islands are important in the oxidation of olefins.

As a result of these considerations, it is considered that a DMA molecule must be adsorbed on a site of two palladium atoms which is also capable of adsorbing a hydrogen molecule, as hydrogen atoms, in close proximity; i.e. a minimum of four adjacent palladium atoms is required. This requires that the reaction cannot take place on sites involving gold atoms, under reaction conditions.

The apparent lack of mobility of hydrogen atoms can be explained very easily. Apart from the fact that the affinity of hydrogen for palladium is so great and that the transference of a hydrogen atom from a palladium site to a gold site is unlikely, it is known that the coverage of hydrogen on gold, at any temperature, is small and that any hydrogen atoms on gold, under the reaction conditions would tend to desorb as molecules very rapidly. Hence the apparent lack of mobility.

The relative strengths of the chemisorption bonds of DMA to palladium and gold can also fit in well with this proposed mechanism. There can be little doubt that DMA is very much more strongly adsorbed on palladium than on gold. This infers that thetrue activation energy of the reaction is very much higher on palladium than it is on gold, but that the frequency factor is enormously higher on palladium. This is a very acceptable picture, the higher activation energy being due to a more stable reaction intermediate/

intermediate etc. Since the apparent activation energy does not change over the alloy range, this mechanism seems even more probable with a picture of DMA molecules being adsorbed on palladium atoms very strongly, and then being attacked by hydrogen atoms on a palladium "island", appearing to be a very attractive explanation.

Just why the surface palladium atoms should not be affected by the bulk properties of the alloy is perhaps not too difficult to explain. The alkyne bond consists in effect, of a large dense electron cloud and in the case of DMA, this density is increased by electron donation from the methyl groups. The DMA bonds itself to the surface by means of donation from this mass of charge. Now a surface atom cannot be truly considered as typical of the atoms in the alloy system; it is in a different environment, partly immersed, as it were, in a completely contrasting electron system. Is it then practical to assume the properties of this location are unaltered? Previous work on palladium-gold alloy catalysts has generally indicated that bulk properties do affect the surface, but the adsorbed gas molecules have not, in these cases, been adsorbed nearly so strongly, nor do they possess such a large dense electron cloud as does DMA which is, of course, a key factor in its adsorption. It is of interest to note that oxygenation reactions, involving, obviously, oxygen which is not adsorbed by gold in any way are difficult to really explain in terms of bulk electronic properties: a difficulty which has, as indicated, been noted by Gerberich (105).

It is suggested then that palladium atoms involved in the hydrogenation of DMA are behaving much more as perhaps palladium atoms in a discrete compound/

compound, (maybe a metal cluster compound) would, and not as part of a homogeneous bulk system.

The action of hydrogen as a poison for the reaction is readily explicable in terms of island sites, since obviously it would be difficult for a DMA molecule to adsorb on an island which was already fully loaded with hydrogen. Quite a small coverage of hydrogen would be sufficient to lower the number of suitable sites for subsequent DMA hydrogenation reactions significantly.

Previous work on catalytic acetylene hydrogenation has indicated two mechanisms which may occur, one involving stepwise addition of atomic hydrogen and the second involving reaction of a chemisorbed acetylene molecule with a physically adsorbed hydrogen molecule and possible subsequent reversal to give either chemisorbed hydrogen atoms or maybe an olefinic species on another site. For alkyl acetylenes only the first proposed mechanism has been observed (see Chapter 1) and all the available evidence in this case points to a stepwise addition of atomic hydrogen to an adsorbed DMA molecule. It seems probable that the DMA and hydrogen molecules must be chemisorbed in close proximity and that subsequently the hydrogen atoms are added stepwise to the DMA. An interesting experiment would be to hydrogenate DMA with an unequilibrated mixture of hydrogen and deuterium molecules over an alloy containing a low concentration of palladium. If this mechanism is correct, then an unusual distribution of deuterated butenes would be produced having high concentrations of d_o and d_2 species, and unusually low concentrations of d_1 butenes. The normal observable results, however, of DMA hydrogenation over/

over these alloys would tie in very well with previous observations for alkyl acetylene hydrogenation, i.e. simple stepwise addition. The mechanism discussed in Chapter 4, for the reaction on gold films, must obviously be different, demanding much more information before any definite conclusion may be drawn.

6.6 Some Notes and Comparisons with Previous Work

a) Palladium-Gold Alloys:

The most directly related work in this field is that of Eley and various co-workers using palladium-gold alloy wires (85,86,87,88). The work of Couper and Eley (85) on para-hydrogen conversion over alloy wires is explicable in terms of the bulk properties of the alloys, but such a system involving palladium with only hydrogen gas, cannot be said to be typical or representative. Other work, such as the decomposition of formic acid (86) the oxidation of carbon monoxide (87) and the decomposition of nitrous oxide (88) does not fit into the pattern so well. For instance, the oxidation of carbon monoxide on gold rich alloys has an apparent activation energy of some 2 k.cal. $mole^{-1}$ whereas that on palladium rich alloys is about 30 k.cal. $mole^{-1}$; there is no reaction on pure gold. It is tempting to suggest that on gold rich alloys some reaction involving palladium islands occurs, since gold does not adsorb oxygen and the heat of adsorption of carbon monoxide on gold is 9 k.cal. $mole^{-1}$. Perhaps oxygen, which will be more strongly adsorbed on palladium than carbon monoxide, is adsorbed on palladium sites in some active form from which it can attack physically adsorbed carbon monoxide. Possibly some chain reaction could produce the oxygen, i.e. via adsorbed O_3 species or O atoms. The other two systems tend to be a little more complex. Formic acid decomposition/

decomposition is basically, of course, a dehydrogenation reaction. Nitrous oxide decomposition is very complex. This work, and that of Inami, Wood and Wise (124) who showed that oxygen which will oxidise 1-butene to 1,3 butadiene in the range 0 - 40 atoms% palladium but not thereafter, is not available in large quantities on the surface.

As already mentioned, Gerberich et al (105) studying the oxidation of ethylene concluded that palladium clusters may be needed for this reaction, thereby suggesting that gold acts only as a diluent to the palladium surface.

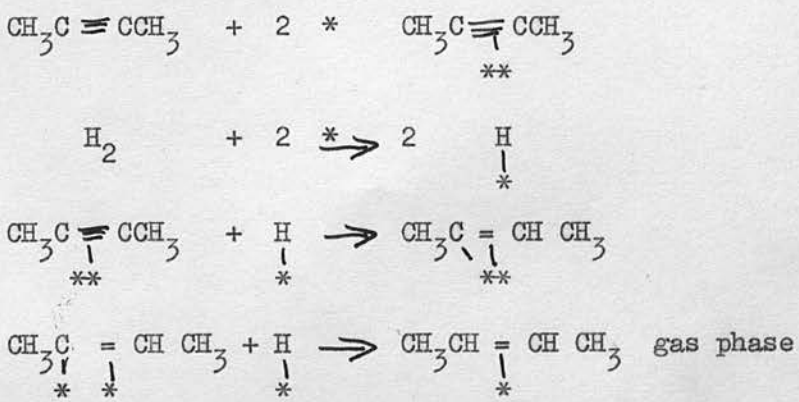
b) Acetylene Hydrogenation:

The work of Hamilton and Burwell (60) and of Meyer and Berwell (59,61) on the hydrogenation of alkyl and dialkyl acetylenes over supported palladium catalysts corresponds well with the results for pure palladium and palladium rich alloys, giving virtually a single product; i.e. high selectivity at near room temperature but selectivity tending to decrease as the temperature increased, probably a thermodynamic effect.

Palladium generally seems to be a very selective catalyst for the hydrogenation of acetylenes which may indicate that some very stable, sterically fixed intermediate is formed, as suggested earlier. Deuteration of DMA over supported palladium (61) gives very selectively cis-but-2-ene, $2,3,d_2$.

In view of palladium's greater selectivity, it is perhaps surprising that nickel with its similar outer electronic structure is much less selective as shown by Mann and co-workers (65,66,68,71,72), the selectivity of/

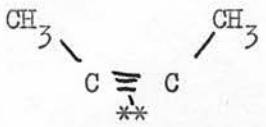
of nickel, unlike that of gold, being independant of alkyne concentration, but decreasing as the hydrogen concentration is decreased. Mann and Khulbe's work on the hydrogenation of methyl acetylene, over copper-nickel alloy powders showed that unlike the related palladium-gold alloys, selectivity increases as the concentration of the "sp" metal increases. Similarly, though, on both alloys polymerisation showed a tendency to increase. On copper-nickel, activation energy varies little, until high concentrations of copper are reached, when it rises sharply. It is tempting to think that this may coincide with the formation of a copper acetylide type of bond on the surface. The activity of the catalysts at first increases sharply as copper is added to the nickel, but then decays in a manner reminiscent of the palladium-gold alloys. The results for copper-nickel reported in this paper are by no means at total variance with those reported here for palladium-gold. Mann and Khulbe's work using palladium catalysts for methyl acetylene hydrogenation (69) fits in with this work quite well, and the stepwise mechanism proposed there and in (71) would agree with the mechanistic ideas outlined earlier so that for DMA the reaction would proceed as follows:



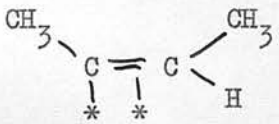
The stereochemistry of this reaction is worthy of comment.

The/

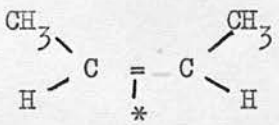
The methyl group is a bulky species, especially in contrast to a hydrogen atom. If the DMA is adsorbed on to the surface by means of a π-bond, then almost certainly electronic and steric considerations indicate that a species of the following type will develop.



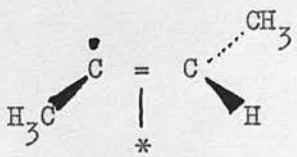
i.e. the methyl groups will be in a cis configuration. The same considerations indicate that the half hydrogenated state, will have the following configuration:



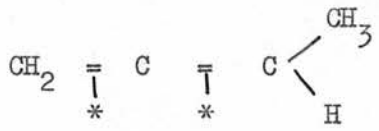
which on further addition of a hydrogen atom will yield adsorbed cis-but-2-ene:

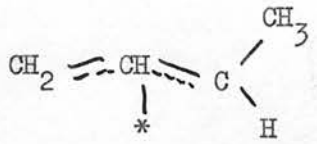


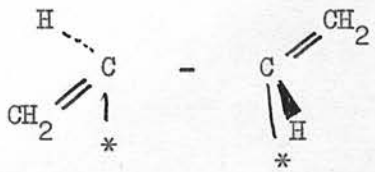
which will desorb to give the major product. Alternative half hydrogenated species such as



planar, and parallel to the surface, would give the trans product on further hydrogenation, as could species such as:







evidence for the occurrence of which is well established, both in other work and in this. Hydrogenation of this could give either but-1-ene or cis-but-2-ene.

With regard to the quantities of DMA isomers produced on higher gold content alloys, it is possible that these are produced by the adsorption of DMA on three palladium atom sites which, by initial hydrogen abstraction from a methyl group and subsequent rearrangement could produce either of the diene products. Since there is no adjacent site available for hydrogen adsorption subsequent hydrogenation would be unlikely to occur. It was noted earlier that maximum polymerisation; presumably due to 1,3 butadiene; occurred in the middle range of the alloys. It may be that in this case, the isomerisation sites occur close enough for subsequent reaction of the diene. This infers that only one gold atom would occur between suitable isomerisation sites.

6.7/

6.7 Final Remarks

In conclusion, it must be said, that in this work, two distinct reactions have been investigated:

i) The reaction of DMA with hydrogen over palladium catalysts

ii) The reaction of DMA with hydrogen over gold catalysts.

It seems probable that these are two distinct reactions separated by the nature of the two metals, one very typically a transition metal and the other an almost perfect "sp" type. In both cases it seems that the strongly adsorbed DMA is attacked by hydrogen, in the case of palladium, almost certainly in the adsorbed atom form. On gold, however, in view of the low affinity of that metal for hydrogen, one is tempted to think in terms of an attack by physically adsorbed hydrogen molecules.

In either case, the overall effect is the stepwise addition of hydrogen atoms. It seems unlikely that reversal of the initial hydrogen addition is important.

Palladium has demonstrated its unusual properties with respect to hydrogen, especially the poisoning effect. It has also demonstrated its amazingly high selectivity. Pure palladium wires and films. hydrogenated DMA to cis-but-2-ene, solely. Gold has proved once more that, although not catalytically very active, it is possessed of unusual properties.

The alloys have indicated that when they adsorb DMA, surface palladium atoms are no longer part of the bulk system, but are effectively part of a palladium-DMA complex.

This/

This work has left a large number of unanswered questions, as perhaps any satisfactory piece of research should. Time, however, prevents further investigation now. Further research into the hydrocracking reaction on gold and into the hydrogenation reaction on gold and high gold content alloys would be indicated. The role of hydrogen in the reaction on palladium rich alloys is also one which needs some clarification. The results of the research into the properties of the alloy catalysts depends probably on the ability of the DMA molecule to form a very stable bond with the palladium, almost extracting it from the bulk catalyst, and demanding subsequent reaction. It may be difficult to find another system with these properties but, if possible, it should be done. Acetylenes can form very stable bonds with other transition metals e.g. iridium, and perhaps one of these could be used.

Finally I would say that anyone attempting such research would be well advised to utilise catalysts in some other form than the wire, the activation of which seems to be an art rather than a science.

The poet, Donne (140) probably summarised the research workers experience when he wrote, in the early 17th century:

"And as no chymique yet th' Elixar got,
But glorifies his pregnant pot,
If by the way to him befall
Some odoriferous thing or medicinall."

APPENDIX

The Arrhenius Equation:

The velocity constant (k) of a reaction is given by

$$k = Ae^{-E/RT}$$

where E is the energy of activation

R is the gas constant

T is the absolute temperature

A is the so-called frequency factor

$$\therefore \quad \log_{10} k = \log_{10} A - \frac{E}{RT \times 2.303}$$

$\therefore$ from a graph of $\log_{10} k$ va. $\frac{1}{T}$

E and A can be calculated.

In the case of the palladium-gold alloys E was constant for the whole range, indicating that A was the sole variable, apart from k and T. This means that there is unlikely to be any compensation effect, indicating that some normal surface structure is involved which does not depend on crystal faults or diffusion processes. In this particular case then, comparison of the frequency factors over the alloy range is unusually interesting.

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